A solution of this Diels-Alder adduct **13** (27 mg, 0.091 mmol) in 0.2 mL of dry dimethylformamide was treated with pyridinium dichromate[21] (102 mg, 0.27 mmol) at 0 °C and the mixture was allowed to stir at room temperature for 9 h. The reaction mixture was poured onto 60 mL of 5% HCl and extracted with ether. The combined extracts were concentrated in vacuo. The crude carboxylic acid was taken up in ether and treated with excess diazomethane at 0 °C, and the mixture was allowed to stir at room temperature overnight. Chromatography (PCTLC, 1 mm SiO_2, 50% ether-hexane eluant) afforded 15 mg (29 mg theoretical, 52%) of **14** as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 7.75-7.25 (m, 5 H), 5.95 (m, 2 H), 4.6 (broad m, 1 H), 4.15 (broad m, 1 H), 3.65 (s, 3 H), 2.8-1.5 (broad m, 9 H); EIMS, m/e 327 (M^+), 131, 105, (base), 91, 77, 68; HRMS, m/e 327.1477, $C_{19}H_{21}NO_4$ requires 327.1469.

14 from 7. A solution of the ester **7** (90 mg, 0.33 mmol) in 1 mL of dry mesitylene and 3 mL of condensed 1,3-butadienes in a resealable Carius tube was heated in a sand-packed lead pipe with a heating mantle at 130-140 °C for 48 h. The reaction tube was cooled to -78 °C and the contents transferred to a round-bottom flask and concentrated in vacuo. Chromatography (SiO_2, 50% ether-hexane) afforded 75 mg (108 mg theoretical, 70%) of pure **14** as a single stereoisomer identical in all respects with material prepared from **2**.

Chemical Correlation of 3 with 8 via 17. 17 from 3. Following the procedure detailed for the conversion of **2** to **14**, **3** afforded **17** in an unoptimized 12% overall yield. **17**: ^1H NMR ($CDCl_3$) δ 7.75-7.25 (m, 5 H), 5.9 (m, 2 H), 4.85 (broad m, 1 H), 3.95 (broad s, 1 H), 3.70 (s, 3 H), 2.8-1.5 (m, 9 H); IR (film) ν_{max} 3044, 3005, 2953, 1734, 1626, 1576, 1452, 1433, 1294, 1279, 1211, 1161, 987 cm^{-1}; EIMS, m/e 327 (M^+), 190, 131, 105 (base), 91, 77; HRMS, m/e 327.1468, $C_{19}H_{21}NO_4$ requires 327.1469.

17 from 8. A solution of **8** (70 mg, 0.256 mmol) in 1 mL of dry mesitylene and 3 mL of condensed 1,3-butadiene in a resealable Carius tube was heated in a sand-packed lead pipe with a heating mantle at 130-140 °C for 48 h. The reaction tube was cooled to -78 °C and the contents transferred to a round-bottom flask and concentrated in vacuo. Chromatography (SiO_2, 50% ether-hexane) afforded 53 mg (83 mg, theoretical, 64%) of pure **17** as a single stereoisomer identical in all respects with material prepared from **3**.

(4α,9β,10β)-4-(Benzoylamino)-9-(methoxycarbonyl)-*cis*-Δ^6-1-octalone Ethylene Ketal (19). A stirred solution of **14** (629 mg, 1.92 mmol) in 9.6 mL of MeOH at room temperature, was treated with 9435 mg of Na/Hg (8%, 15 weight equiv)[22] and allowed to stir for 1.5 h. The reaction mixture was filtered through Celite and the filtrate poured over water and extracted with EtOAc. The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (SiO_2, EtOAc eluant) afforded 425 mg (625 mg, theoretical, 68%) of alcohol **18**: ^1H NMR ($CDCl_3$) δ 7.85-7.25 (m, 5 H), 7.00-6.70 (m, 2 H), 6.0-5.5 (m, 2 H), 4.35-3.9 (m, 1 H), 3.8 (s, 3 H), 3.2-1.75 (m, 8 H); EIMS, m/e 329 (M^+), 297, 269, 230, 208, 180, 158, 148, 132, 122, 105 (base), 91, 77; HRMS, m/e 329.16395, $C_{19}H_{23}NO_4$ requires 329.16257; IR (KBr) ν_{max} 3408, 1720, 1647, 1578, 1487, 1414, 1385, 1346, 1321, 1261, 713, 696, 661, 625 cm^{-1}.

A stirred solution of the alcohol **18** (21.5 mg, 0.06 mmol) in 0.3 mL CH_2Cl_2 at 0 °C was treated with PCC[23] (28 mg, 0.13 mmol) and allowed to stir at room temperature for 1.5 h. The reaction mixture was filtered through Celite and the filtrate poured onto 10% HCl and extracted with EtOAc. The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (SiO_2, EtOAc eluant) afforded 15 mg (21 mg theoretical, 71%) of the desired ketone: ^1H NMR ($CDCl_3$) δ 7.8-7.3 (m, 5 H), 6.25-5.95 (m, 1 H), 5.75-5.6 (m, 2 H), 5.0-4.5 (m, 1 H), 3.85 (s, 3 H), 3.0-2.0 (m, 9 H); IR (KBr) ν_{max} 3302, 1718, 1633, 1551, 1242, 1226 cm^{-1}; EIMS, m/e 327 (M^+), 267, 205, 174, 147, 122, 105 (base), 77; HRMS, m/e 327.14674, $C_{19}H_{21}NO_4$ requires 327.14693.

A solution of the ketone (300 mg, 0.91 mmol) in 15 mL of benzene containing 0.1 mL (1.8 mmol, 2 equiv) of ethylene glycol and 17 mg (0.091 mmol, 0.1 equiv) of *p*-TsOH, was allowed to reflux for 6 h with azeotropic removal of water. The crude mixture was then poured over water and extracted with EtOAc. The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (PCTLC, 1 mm, EtOAc eluant) gave 282 mg (340 mg theoretical, 83%) of ketal **19**: ^1H NMR ($CDCl_3$) δ 7.7-7.25 (m, 5 H), 6.85-6.6 (m, 1 H), 5.85-5.4 (m, 2 H), 4.35-4.00 (m, 1 H), 3.8 (m, 4 H), 3.65 (s, 3 H), 3.0-1.5 (m, 9 H); IR (film) ν_{max} 3450, 3025, 2975, 2900, 1720, 1660, 1520, 1480, 1460, 1440, 1260 cm^{-1}; EIMS, m/e 371 (M^+), 326, 250, 200, 191, 105 (base), 86, 77. Anal. Calcd for $C_{21}H_{25}NO_3$: C, 67.90; H, 6.78; N, 3.77. Found: C, 67.52; H, 6.90; N, 3.79.

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Supplementary Material Available: Full details of the X-ray structure determination of **13** (13 pages). Ordering information is given on any current masthead page.

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Reduction of Schiff Bases with Isopropyl Alcohol and Aluminum Isopropoxide in the Presence of Raney Nickel[1]

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The reduction of several *N*-alkyl and *N*-aryl ketimines to the corresponding secondary amines is described. The reaction, which generally proceeds in high yield, is effected by isopropyl alcohol and aluminum isopropoxide in the presence of Raney nickel. In the absence of the nickel catalyst, that is, under the Meerwein-Ponndorf-Verley conditions, the reaction takes a different route and *N*-isopropylamines are formed at preference to the direct reduction products. Without the aluminum alkoxide the reduction proceeds only for a small percentage. This reaction, besides offering a new method for the synthesis of secondary amines, represents the first example where the couple aluminum alkoxide/Raney nickel is used in catalytic transfer hydrogenation reactions.

We have been interested for many years in the system alcohol, aluminum alkoxide, and Raney nickel as alkylating agent of indoles,[2,3] pyrroles,[3] and amines.[4] In particular, in a recent paper,[1] we described some mechanistic aspects

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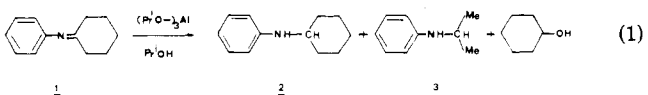
of the N-alkylation of amines by reaction with alcohols, catalyzed by aluminum alkoxide and Raney nickel. In that report we suggested that the N-alkylation proceeds by the intermediate formation of ketimines, the latter compounds arising from the condensation of the primary amines and the carbonyl compounds formed along the reaction course, as the oxidation products of the alcohols. Subsequent reduction of the ketimines affords the N-alkylation products.

In the past much work has been devoted to the reduction of azomethine compounds to the corresponding amines. This reaction is effected by various reagents such as hydrides,[5] diborane,[6] dissolved metals,[7] formic acid,[8] sodium dithionite,[9] and hydrogen over metal catalysts.[10] Although the reduction of imines is generally said to be very easy and readily performed with various reducing agents,[10,11] only few and scattered examples are reported for the homogenous reduction of *N*-alkyl and *N*-aryl ketimines, and even in these cases yields are generally not satisfactory.[5b,9,12] Moreover, to our knowledge, only two papers deal with catalytic-transfer hydrogenation of aldimines by use of rhodium or ruthenium complexes.[13]

The aim of the present investigation is to support the existence of ketimines as intermediates of the N-alkylation process of primary amines, performed by alcohol/aluminum alkoxide/Raney nickel, and, mainly, to study this catalytic system as a reagent for the reduction of the carbon–nitrogen double bond in ketimines. We also report that such a reduction generally proceeds well and serves as a convenient method to convert unhindered *N*-alkyl and *N*-aryl ketimines to the corresponding amines.

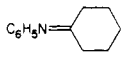
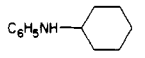
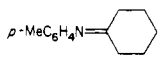
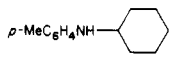
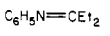
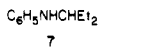
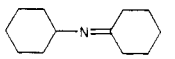
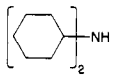
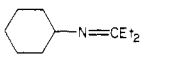
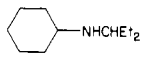
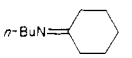
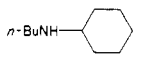
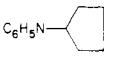
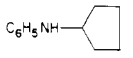
Results and Discussion

The first approach we employed was to try the reduction of *N*-cyclohexylideneaniline (1) under the Meerwein–Ponndorf–Verley conditions,[14] that is by treatment with aluminum isopropoxide in the presence of isopropyl alcohol (eq 1). The reaction was very slow and went to completion only with a large amount of isopropyl alcohol, but large quantities of *N*-isopropylaniline (**3**) were produced.



(1)

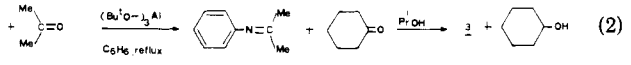
Table I. Reduction of *N*-Alkyl and *N*-Aryl Ketimines with Isopropyl Alcohol, Aluminum Isopropoxide, and Raney Nickel

substrate	time, h	product	% yield[a]
 1	1	 2	80
 4	1.5	 5	83
 6	12	 7	82
 8	24	 9	50
 10	19	 11	72
 12	18	 13	66
 14	48	 15	20

[a] Yields are given for the pure compounds obtained after distillation; no other products were present in the crude reaction mixture.

In a typical experiment in fact, with 3 mol of aluminum isopropoxide in isopropyl alcohol as the solvent, after 3 days, no more starting material 1 was present in the reaction mixture and only 3% of the reduction product **2** was formed as well as 59% of *N*-isopropylaniline (**3**) and 38% of cyclohexanol (GC peak areas). Similar results were obtained by using different substrates, solvent systems (*tert*-butyl alcohol, benzene, xylene), and reagent concentrations. This result can be due to the presence of acetone, firstly produced as the oxidation product of isopropyl alcohol by the initial *N*-cyclohexylideneaniline reduction. In the sequel, at the presence of the acid catalyst, acetone reacts with the ketimine to exchange the carbonyl residue,[15] yielding *N*-isopropylideneaniline which is readily reduced to **3**.[16]

In order to prove this mechanistic hypothesis we allowed 1 to react with acetone in the presence of aluminum *tert*-butoxide in benzene.[17] Once *N*-isopropylideneaniline and cyclohexanone were formed (GC–MS analysis), isopropyl alcohol was added. **3** and cyclohexanol were the ultimate products of the reaction (see eq 2).



(2)

On the other hand the alternative route, passing through the ketimine hydrolysis, promoted by traces of water present in the reaction mixture and subsequent aniline alkylation, was ruled out. In fact, attempts to directly alkylate aniline with isopropyl alcohol and aluminum isopropoxide failed.

At this stage, it seemed to us reasonable that also in the ketimine reduction process Raney nickel could play an important role. The reduction reaction was thus attempted under the same conditions used for the amines N-alkylation reaction.[4] As expected, the use of W-2 Raney nickel, in addition to isopropyl alcohol and aluminum isopropoxide, caused a major improvement. Thus, treatment of 1 in refluxing xylene for 1 h with 2.5 mol of aluminum isopropoxide, 3 mol of isopropyl alcohol, and W-2 Raney

(1) This paper is part 3 in the series "Alcohols and Aluminum Alkoxides in the Presence of Raney Nickel as Alkylating Agents"; Part 2: De Angelis, F.; Ferretti, G.; Botta, M.; Grgurina, I.; Nicoletti, R. *Gazz. Chim. Ital.* **1982**, *112*, 267.

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(17) Aluminum *tert*-butoxide instead of aluminum isopropoxide was used in order to avoid the direct reduction of the ketimines.

nickel (50% w/w of the substrate) afforded the required *N*-cyclohexylaniline (**2**) in 80% yield (isolated product, after distillation). When Raney nickel was replaced by palladium on charcoal, palladium on barium sulfate, or powdered nickel, the composition of the reaction mixture was similar to that obtained when performing the reaction without the catalyst.

The same reaction was then extended to other *N*-alkyl and *N*-aryl ketimines prepared by using modifications of literature methods (see the Experimental Section). As summarized in Table I, except one case, yields were good to excellent. As far as the *N*-cyclopentylideneaniline (**14**) reduction is concerned (entry 7), the low yields could be due to the starting material which probably undergoes condensation in the presence of the aluminum alkoxides. Unvolatile materials in fact remain after the product distillation. This fact, however, was expected: at difference to most ketones, cyclopentanone fails to give high yield in the Meerwein–Ponndorf–Verley reduction,[18] this being explained in terms of mesityl type condensation of the ketone under the reaction conditions.[14] Steric hindrance restricts the range of applicability of the reaction. Carvone anil in fact does not undergo reduction (also the diminished nitrogen basicity could be responsible for this), while reduction of *N*-(1,3-dimethylbutylidene)benzylamine (**16**) is very sluggish, only 10% of the reduction product (GC–MS analysis) being formed after 48 h.[19]

The necessity of the combined action of Raney nickel and aluminum isopropoxide has also been investigated. Raney nickel alone (50% w/w of the substrate) is also able to effect reduction of the ketimine to the corresponding amine but the reaction proceeds only for a small percentage (10–5% for the reduction of **1** and *N*-cyclohexylidene-*p*-toluidine (**4**)), probably just comsuming the amount of hydrogen absorbed on the catalyst. On the other hand the role of the aluminum alkoxide could not be exclusively that of regenerating the Raney nickel activity. Steric hindrance at the reaction center in fact prevents the ketimine reduction, this being an indication of coordination between the substrate and aluminum isopropoxide along the reaction course. To this point we can only speculate that probably the reduction occurs on the catalyst surface, where both the hydrogen absorbed on it and the hydrogen donor can play a part.

It is worth pointing out that reactions making use of the concomitant action of hydride donors and Raney nickel are not unusual,[20] but, to our knowledge, this is the first description of the use of the couple aluminum alkoxide/Raney nickel in such catalytic-transfer hydrogenation reactions.[21] Moreover, the reaction described, represents a mild and generally high yielding method for reducing *N*-alkyl and *N*-aryl ketimines to the corresponding secondary amines. Finally, the plausible existence of ketimines along the reaction path of the N-alkylation of amines by alcohols and aluminum alcoxides in the presence of Raney nickel[1] is also confirmed.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer. ^{1}H NMR spectra were determined on a Varian EM 360 A instrument ($CDCl_3$ as solvent and Me_4Si as internal standard were used). GC analyses were performed on a Hewlett-Packard 5880 A instrument (N_2 as carrier), fitted with a 3 m, 4% OV 17 on chromosorb G 80–100 mesh column. Preparative GC was performed on a Carlo Erba Fractovap GV instrument (N_2 as carrier) fitted with a 2 m, 6% SE 52 on chromosorb W 80–100 mesh column. Mass spectra at 55 eV coupled with gas chromatographic analyses were performed on a Kratos MS 80 spectrometer interfaced with a Carlo Erba Fractovap series 4160 gas chromatograph (He as carrier), fitted with a 2 m, 3% SP 2250 on Supelcobort 100–120 mesh glass column. High resolution mass measurements were taken on the Kratos instrument (RP 10 000). Refractive indices were taken on a Bausch and Lomb Abbe refractometer.

Table II. Synthesis of Ketimines

no.	method	% yield	bp, °C (mmHg)	lit. bp, °C (mmHg)	n^{20}_D
1	A	69	148–149 (25)[d]	157 (30)[26]	1.5593
4[a]	A	86	98–99 (0.2)		1.5543
6[b]	B	83	58–60 (0.4)	110–111 (20)[27]	
8	B	71	138–140 (22)[d]	135–137 (20)[28]	1.4977
10[b]	B	52	93–95 (1.5)		
12[b]	B	55	125–126 (28)[d]		
14	c		90–91 (0.4)		
16[a]	A	88	135–140 (20)[d]		

[a] Sensitive to moisture, failed to give elemental analysis. Accurate mass: **4**, calcd for $C_{13}H_{17}N$ *m/e* 187.1360, found 187.1367. **16**, calcd for $C_{12}H_{17}N$ *m/e* 175.1361, found 175.1359. [b] For details about identification, see the Experimental Section. [c] Cyclopentanone and aniline failed to give cyclopentylideneaniline (**14**) following both methods A and B; **14** has been synthetized according to a new procedure, by our laboratory, which will be published in due course. [d] During distillation, a $CaCl_2$ trap was used in order to avoid moisture.

Freshly prepared Raney nickel W-7,[22] stored under absolute ethanol and weighed as settled catalyst, was washed with dry xylene before use. Solvents and isopropyl alcohol were distilled from sodium metal before use. Commercially available aluminum isopropoxide was distilled before use. Ketimines were prepared by using modifications of the literature method.[23] The $ZnCl_2$·amine complex, used for the synthesis of some ketimines (vide infra), was prepared according to the literature method.[24] Carvone anil was prepared according to the literature.[25]

Ketimine Preparations. Method A. The ketone (0.1 mol) and the amine (0.1 mol) were refluxed in xylene (100 mL) in the presence of $ZnCl_2$ (1.36 g, 10 mmol) for 24 h, water being removed by azeotropic distillation. After cooling at 80 °C the precipitated solid was removed by filtration at that temperature. The filtrate was then evaporated in vacuo (a $CaCl_2$ trap was used in order to avoid moisture). The crude product was then purified by distillation. The experimental details are summarized in Table II. Spectral data of previously undescribed ketimines are given below.

Method B. Reactions were performed in 50-mL sealed Pyrex vials. A solution of the amine (58 mmol), the ketone (58 mmol, 116 mmol for diethyl ketone), and the $ZnCl_2$·amine complex (1.24 mmol) were heated at 180 °C for 48 h; at the beginning stirring was necessary in order to dissolve the complex. After cooling, the crude mixture was first distilled at atmospheric pressure in order to remove volatiles, and then the residue distilled at reduced pressure to give the pure products. The experimental details are summarized in Table II. Spectral data of previously undescribed ketimines are given below. Spectra of *N*-(1-ethylpropylidene)-cyclohexylamine (**10**) and of *N*-cyclohexylidenebutylamine (**12**) have not been taken because they are readily hydrolized by traces of water; they have been directly reduced after distillation. **6** also is very sensitive to moisture and failed to give any reliable elemental analysis or mass spectrum.

Spectral Data of Ketimines. *N*-Cyclohexylidene-*p*-toluidine (4): IR (CCl_4) 1655 (C=N) cm^{-1}; NMR δ 7.3–6.2 (4 H, AA′XX′ system, aromatic), 2.67–1.90 (4 H, m, N=C(CH_2)$_2$, 2.23 (3 H, s, CH_3), 1.9–1.0 (6 H, m); MS, *m/e* (relative intensity) 187 (M^+, 50), 144 (100), 131 (15), 91 (20).

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Table III. Ketimine Reduction. Physical Constants of the Products

no.	bp, °C (mmHg)	n^{20}_D	lit. data
2	76–80 (0.1)[a] 167–168 (20)	1.5477	bp 167 °C (20 mmHg)[29]
5	82–85 (0.2)[a,b]		mp 42–42.5[30] °C
7	70–71 (1.5)[a]	1.5300	$n^{18.5}_D$ 1.5303[31]
9	145–146 (38)[a]	1.4846	n^{25}_D 1.4830[32]
11	110–120 (34)[a] 209–210 (760)	1.4548	bp 208–209 °C (760 mmHg)[33]
13	110–120 (35)[a] 208–209 (760)		bp 207 °C (760 mmHg)[34]
15	60–61 (1.5)[a] 265–266 (760)		bp 266 °C (760 mmHg)[35]

[a] Product distilled in a Hickmann apparatus; bath temperature given. [b] mp 42–43 °C.

***N*-(1-Ethylpropylidene)aniline (6)**: IR (film) 1655 (C=N) cm^{-1}; NMR 7.2–6.2 (5 H, m, aromatic), 2.06 (4 H, q, J = 8 Hz, CH_2), 0.90 (6 H, t, J = 8 Hz, CH_3).

***N*-(1,3-Dimethylbutylidene)benzylamine (16)**: IR (CCl_4) 1660 (C=N) cm^{-1}; NMR δ 7.20 (5 H, s, aromatic), 4.43 (2 H, s, CH_2N), 2.26 (2 H, d, J = 9 Hz, $=CCH_3$), 1.86 (3 H, s, $=CCH_3$), 1.5–1.3 (1 H, m), 0.95 (6 H, d, J = 7 Hz); MS, m/e (relative intensity) 189 (M^+, 3), 174 (8), 147 (65), 132 (6), 91 (100).

Treatment of *N*-Cyclohexylideneaniline (1) with Isopropyl Alcohol and Aluminum Isopropoxide. A solution of 1 (200 mg, 1.16 mmol) and aluminum isopropoxide (710 mg, 3.48 mmol) in isopropyl alcohol (20 mL) was refluxed for 3 days. The mixture was then concentrated under vacuum; Et_2O (80 mL) and 5% NaOH (80 mL) were added. The aqueous layer was then extracted three times with Et_2O; the combined organic extracts were washed with H_2O and with brine, dried (Na_2SO_4), and evaporated in vacuo to give the crude product (160 mg) which was analyzed by GC–MS. By comparison of the peak retention times and the mass spectra with those of authentic samples, the crude product showed to be a mixture of cyclohexanol (38%), *N*-isopropylaniline (3) (59%), and *N*-cyclohexylaniline (2) (3%) (percentages were based on GC peak areas).

Treatment of *N*-Cyclohexylideneaniline (1) with Acetone and Aluminum *tert*-Butoxide and Subsequent Reduction of *N*-Isopropylideneaniline with Isopropyl Alcohol. *N*-Cyclohexylideneaniline (1) (100 mg, 0.58 mmol) was treated with dry acetone (from $CaCl_2$, 0.13 mL, 1.74 mmol) in refluxing xylene (10 mL) in the presence of aluminum *tert*-butoxide (430 mg, 1.74 mmol) for 18 h. An analytical sample was treated with a few drops of ethyl acetate and directly injected for GC–MS analysis. The solution showed to be a mixture of 1 (10%), cyclohexanone (35%), and *N*-isopropylideneaniline (55%) (percentages are based on GC peak areas). MS of *N*-isopropylideneaniline, m/e (relative intensity) 133 (M^+, 100), 118 (98), 77 (82).

Isopropyl alcohol (20 mL) was then added to the reaction mixture and heating was continued for an additional 8 h. Usual workup (vide supra) and GC–MS analysis of the crude product showed the exclusive presence in the reaction mixture of cyclohexanol and *N*-isopropylaniline (3).

Treatment of Aniline with Isopropyl Alcohol and Aluminum Isopropoxide. A solution of aniline (100 mg, 1.07 mmol) and aluminum isopropoxide (175 mg, 0.85 mmol) in isopropyl alcohol (15 mL) was refluxed for 20 h. A GC analysis of the crude reaction mixture showed the exclusive presence of the starting material.

Ketimine Reduction with Isopropyl Alcohol, Aluminum Isopropoxide, and Raney Nickel. General Procedure. A solution of the substrate (10 mmol) in xylene (125 mL) and isopropyl alcohol (2.28 mL, 30 mmol) was vigorously stirred under reflux for the appropriate time (see Table I) in the presence of aluminum isopropoxide (5 g, 25 mmol) and Raney nickel (50% w/w of the substrate). The cooled reaction mixture was diluted with Et_2O (60 mL) and aluminum complexes were decomposed with 5% NaOH (40 mL), Raney nickel being suspended in the aqueous layer. After separation, the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic extract were treated with 2 N HCl (3 × 40 mL); alkalinization of the acid layer with 30% NaOH and extraction with Et_2O (3 × 50 mL) followed. The combined organic layers were washed with H_2O and brine and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the crude products which were then purified by distillation. For analytical purposes *N*-cyclohexylbutylamine (13) and *N*-cyclopentylaniline (15) were ultimately purified by preparative GC. Reaction products are all known. The experimental details and physical constants are summarized in Table III; yields are given in Table I.

As to the reduction of carvone anil, it was recovered unchanged after 48 h, while, after the same reaction time, 16 was reduced to an extent of 10% (product not isolated, GC peak area) to *N*-(1,3-dimethylbutyl)benzylamine: MS, m/e (relative intensity) 191 (M^+, 0.5), 186 (6), 134 (72), 91 (100).

Treatment of 1 and 4 with Raney Nickel. Separate experiments were performed. The substrate (1 mmol) was refluxed in xylene (9 mL) and isopropyl alcohol (0.23 mL, 3 mmol) in the presence of Raney nickel (50% w/w of the substrate). After 1.5 h the catalyst was filtered off and the crude mixture analyzed by GC. The amine 2 was present in 10% yield and the amine 5 in 5% yield, the remaining being the starting material (GC peak areas).

Registry No. 1, 1132-38-3; 2, 1821-36-9; 3, 768-52-5; 4, 36132-68-0; 5, 10386-93-3; 6, 38425-96-6; 7, 2810-72-2; 8, 10468-40-3; 9, 101-83-7; 10, 6125-73-1; 11, 51609-04-2; 12, 6407-39-2; 13, 10108-56-2; 14, 13683-42-6; 15, 40649-26-1; 16, 60307-45-1; isopropyl alcohol, 67-63-0; aluminum isopropoxide, 555-31-7; nickel, 7440-02-0; cyclohexanone, 108-94-1; 2-butanone, 78-93-3; 4-methyl-2-pentanone, 108-10-1; aniline, 62-53-3; *p*-toluidine, 106-49-0; benzylamine, 100-46-9; zinc dichloride, 7646-85-7; *N*-isopropylideneaniline, 1124-52-3; acetone, 67-64-1; aluminum *tert*-butoxide, 556-91-2.