corresponding oxirane.[48] On the other hand, aldol-type condensations of α-bromo ketones with aldehydes have been performed with the corresponding stannous enolates, but the subsequent production of α,β-epoxy ketones required an additional treatment with base.[49]

## Experimental Section

All reactions were performed in thoroughly dried (110 °C) glassware under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl. $^1$H NMR spectra were measured with a Varian T-60 NMR spectrometer, while $^{13}$C NMR spectra were obtained with a Varian FT 80 NMR spectrometer. IR spectra were performed with a Perkin-Elmer Model 1310 spectrophotometer, and mass spectra were measured with a Varian-Mat Model 112 mass spectrometer. Starting α-chloro ketimines **6** were prepared by condensation of a primary amine with an appropriate α-chloro ketone in the presence of titanium(IV) chloride.[23]

**General Procedure for the Synthesis of 2-Imidoyloxiranes 9.** To a solution of lithium diisopropylamide (0.105–0.150 mol) at 0 °C in 150 mL of THF, prepared from *n*-BuLi (0.105–0.150 mol) and diisopropylamine (0.2 mol), was added a solution of α-chloro ketimine **6** (0.1 mol) in 20 mL of THF. The deprotonation was complete after 2 h at 0 °C and then 0.1–0.2 mol of the ketone or aldehyde ($R^2R^3CO$) was added dropwise to the solution of the 3-chloro-1-azaallylic anion **7**. After the addition, the reaction mixture was stirred during several hours (Table I), while the temperature became ambient. The reaction mixture was then poured into water and extracted with ether (3 × 100 mL). The combined extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. More details about the synthesis of the resulting 2-imidoyloxiranes **9** are given in Table I.

**Synthesis of 2-Acyloxiranes 10 (General Procedure).** The reaction mixture, containing pure oxiranes **9**, prepared according to the procedure described above, was hydrolyzed with an aqueous HCl solution (10 equiv of 2 N HCl; room temperature, 1 day) to give, after extraction ($CH_2Cl_2$), drying ($MgSO_4$), and evaporation of the solvent, the oxiranes **10**. These compounds are isolated in pure form via preparative gas chromatographic analysis. The spectral data of compounds **10** are given in Tables III and IV.

**Synthesis of 3-Butenamides 14 (General Procedure).** To a solution of lithium diisopropylamide (0.20 mol) at 0 °C in THF, prepared according to the procedure described above (*n*-BuLi 0.20 mol, diisopropylamine 0.40 mol) was added 1–2 molar equiv of HMPA (Table II). Then, a solution of α-chloro ketimine **6** (0.10 mol) in 20 mL of THF was added dropwise. After complete deprotonation (2 h, 0 °C), 0.1 mol of benzophenone (or a substituted analogue) was added dropwise to the solution, after which the reaction mixture was stirred for several hours (Table II). After being poured into water, the reaction mixture was extracted with $CH_2Cl_2$ (4 × 100 mL). The combined extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. To the residual material was added a mixture of pentane and ether (1:1), and the solution was left in the refrigerator (−20 °C) for several hours. All 3-butenamides **14** are solid compounds and they could be easily isolated by filtration. All isolated 3-butenamides **14** are new compounds and the synthesis and the spectral data are given in Tables II, V, and VI.

**Synthesis of 3-Butenenitrile 25.** The preparation of 3-butenenitrile **25** was performed according to a procedure described in the literature.[32] 3-Butenamide **14b** (R = *t*-Bu) (0.01 mol) was reacted with $POCl_3$ (0.05 mol) in boiling benzene (50 mL) during 6 h. After workup, 3-butenenitrile **25** was isolated (87%) in addition to a small amount of starting material (10%). 3-Butenamide **25** is a new compound, and the spectral data are given in Tables V and VI.

**X-ray Crystallographic Analysis of *N*-Isopropyl-3-methyl-4,4-diphenyl-3-butenamide (14a).** Crystals of 3-butenamide **14a**, suitable for X-ray crystallographic analysis, were obtained from a concentrated solution in chloroform at −20 °C. The crystals of 3-butenamide **14a** (parallelepiped) exhibited crystallographic characteristics, which will be published in a forthcoming publication.

**Registry No.** **6** (R = *i*-Pr, $R^1$ = Me), 78827-36-8; **6** (R = *i*-Pr, $R^1$ = Ph), 78827-43-7; **6** (R = cyclohexyl, $R^1$ = Me), 81815-43-2; **6** (R = *t*-Bu, $R^1$ = Me), 78827-37-9; (*E*)-**9a**, 115797-28-9; (*Z*)-**9a**, 115797-40-5; **9b**, 115797-29-0; **9c**, 115797-30-3; **9d**, 115797-31-4; *cis*-**9e**, 115797-32-5; *trans*-**9e**, 115826-83-0; **9f**, 115797-33-6; **10a**, 14179-56-7; **10b**, 23457-03-6; **14a**, 115797-34-7; **14b**, 115797-35-8; (*Z*)-**14c**, 115797-36-9; (*E*)-**14c**, 115797-37-0; **14d**, 115797-38-1; **25**, 115797-39-2; MeCOMe, 67-64-1; $C_6H_5CHO$, 100-52-7; $C_6H_5CO$-$C_6H_5$, 119-61-9; MeCOEt, 78-93-3; Cl-*p*-$C_6H_4COC_6H_5$, 134-85-0.

**Supplementary Material Available:** Table V describes the $^{13}$C NMR spectral data (δ $CDCl_3$) of oxiranes **9** and **10**, while Table VI presents the $^{13}$C NMR spectral data of 3-butenamides **14** and nitrile **25** (3 pages). Ordering information is given on any current masthead page.

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# A New Synthesis of *N*-Aryl-2-methyleneazetidines

Paul Sulmon,† Norbert De Kimpe,*,‡ and Niceas Schamp

*Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure Links 653, B-9000 Gent, Belgium*

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A novel straightforward synthesis of *N*-aryl-2-methyleneazetidines has been developed by reaction of *N*-aryl β-chloro ketimines with potassium *tert*-butoxide.

## Introduction

2-Methyleneazetidines **1** are a group of strained cyclic enamines for which little information is available.[1,2] The development of their chemistry parallels, to some extent, that of their lower cyclic analogues, i.e., methylene-

**Scheme I**

**1** **2**

† Present address: Laboratory of Chemical Products, DSM Limburg b.v., 6160 MB Geleen, The Netherlands.
‡ Senior Research Associate (Onderzoeksleider) of the Belgian National Fund for Scientific Research (Nationaal Fonds voor Wetenschappelijk Onderzoek).

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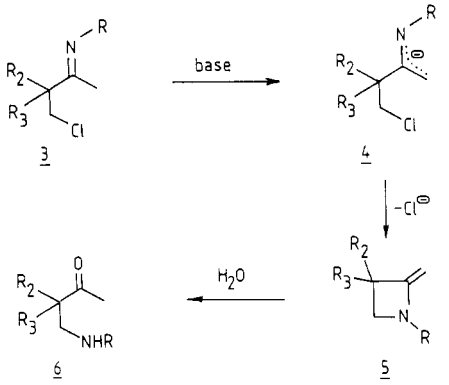
**Table I. Synthesis of 2-Methyleneazetidines 9**

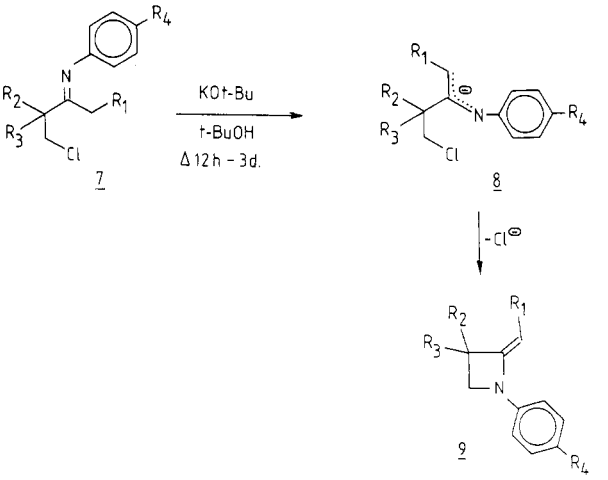
| entry | starting compound | $R_1$ | $R_2$ | $R_3$ | $R_4$ | reaction conditions[a] | yield of 9 (%) | remarks |
|---|---|---|---|---|---|---|---|---|
| 1 | **7a** | H | Me | Me | H | KO-*t*-Bu (2 E)/HO-*t*-Bu, Δ 12 h | **9a**: 90[b] | |
| 2 | **7a** | H | Me | Me | H | KO-*t*-Bu (2 E)/THF, Δ 3 h | **9a**: 90[c] | |
| 3 | **7b** | H | Me | Me | Me | KO-*t*-Bu (2 E)/HO-*t*-Bu, Δ 15 h | **9b**: 87[b] 63[d] | bp 60–65 °C/0.05 mmHg |
| 4 | **7c** | H | Me | Me | Cl | KO-*t*-Bu (2 E)/HO-*t*-Bu, Δ 15 h | **9c**: 95[b] 53[d] | bp 54–60 °C/0.05 mmHg |
| 5 | **7d** | H | $-(CH_2)_5-$ | | H | KO-*t*-Bu (2 E)/HO-*t*-Bu, Δ 3 d | **9d**: 87[b] | |
| 6 | **7e** | $-(CH_2)_3-$ | | Me | H | KO-*t*-Bu (2 E)/HO-*t*-Bu, Δ 2 d | **9e**: 82[b] | |

[a] E = molar equivalents; Δ = reflux; h = hours; d = days; Satisfactory analytical data for compounds **9a**, **9b**, **9c**, and **9d** (±0.3% for C, H, and N) were obtained; all compounds gave $^1H$ and $^{13}C$ NMR data consistent with the structures (some representative examples are given in the Experimental Section). [b] Yield before distillation (purity >97%). [c] Compound **9a** was partially transformed during workup to the corresponding β-arylamino ketone **12** ($R_4$ = H). [d] Yield after distillation. The lower yield is due to partial decomposition during distillation (pure distillate and formation of residual tarry material).

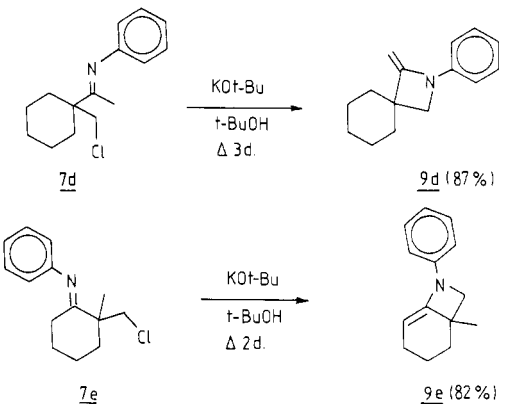
**Scheme II**




**Scheme III**




**Scheme IV**




aziridines **2**, which have recently received increasing interest[3] (Scheme I). A few functionalized 2-methyleneazetidines have been described.[4-14] Polyfluoro-2-methyleneazetidines were prepared by reaction of perfluoroisobutene or substituted ethynes with bis(trifluoromethyl)ketenimines.[4-7,10,11] Some 2-methyleneazetidines were also synthesized by the reaction of *N*-alkylazetidine-2-carboxylates with lithium diisopropylamide followed by the reaction with chlorodimethyl-*tert*-butylsilane,[8-9,12] or by reaction of 2-ethoxyazetinium salts with the sodium salt of ethyl cyanoacetate or malononitrile.[13,14]

## Results and Discussion

Recently we described the reaction of β-chloro imines with bases,[15,16] which lead to different products depending upon the substituent on nitrogen. With *N*-benzyl imines, the intermediate *N*-benzyl-2-azaallyl anion undergoes ring closure to cyclopropylamine derivatives.[15] *N*-Alkyl de-

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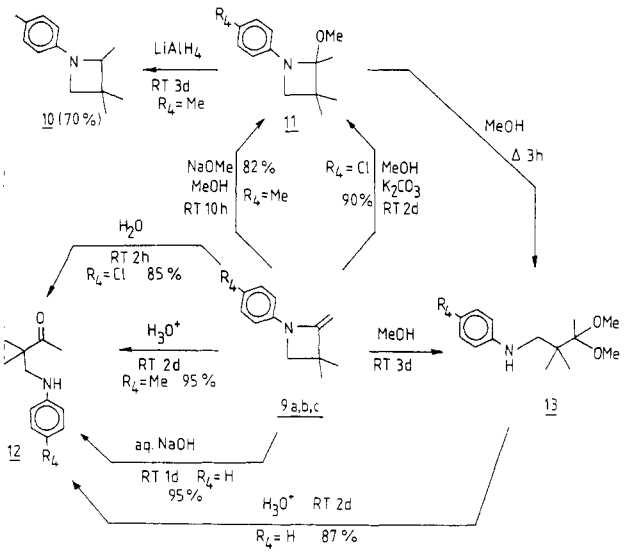
rivatives gave β-(alkylamino) ketones **6** (Scheme II).[16] In this reaction mechanism, 2-methyleneazetidines **5** were postulated as intermediates but could not be isolated under the conditions employed.

Reasoning that the methyleneazetidine would be stabilized by an *N*-aryl substituent, *N*-aryl β-chloro ketimines were subjected to base. This premise was borne out, and we now report the isolation of *N*-arylmethyleneazetidines. Treatment of *N*-aryl β-chloro imines **7** with potassium *tert*-butoxide in *tert*-butyl alcohol afforded *N*-aryl-2-methyleneazetidines **9** in 82–95% yield. The formation of 2-methyleneazetidines **9** occurs by initial deprotonation at the α′-position with the generation of a 1-azaallyl anion **8**. Ring closure by intramolecular nucleophilic substitution of anion **8** produces 2-methyleneazetidines **9** (Scheme III). Compounds **9** are only stable if the substituent on nitrogen is an aromatic group and if the workup procedure excludes water. The latter point refers to treatment of the reaction mixture with pentane, followed by stirring of the reaction mixture, removal of the precipitated material, and evaporation of the solvent at room temperature under vacuo. If the workup of the reaction mixture was performed in the presence of water, 2-methyleneazetidines **9** were partially converted into the corresponding β-(arylamino) ketones **6** (R = Ar) (Table I, entry 2). Thus, 2-methyleneazetidines **5** were always formed during the reaction of β-chloro imines **3** (R = alkyl, aryl) with potassium *tert*-butoxide. If aliphatic substituents are present on nitrogen (**3**; R = alkyl), the intermediate four-membered exomethylene N-heterocycles were converted during workup into the corresponding β-(alkylamino) ketones **6**. All attempts to isolate *N*-alkyl-2-methyleneazetidines were unsuccessful. This new method for the synthesis of 2-methyleneazetidines was also applicable to the preparation of spiro compound **9d** and bicyclic compound **9e**, which proved that the described method entails some generality (Scheme IV).

All 2-methyleneazetidines **9** are new compounds, the synthesis of which is presented in Table I. Concerning the scope and generality of the synthesis of 2-methyleneazetidines, it can be added that all efforts to synthesize β-chloro ketimines lacking geminal α,α-disubstitution met with no success. Accordingly, at present, the synthesis of 2-methyleneazetidines via β-chloro imines is limited to substrates having a geminal dialkyl substitution. Since few 2-methyleneazetidines are known in the literature, their chemistry has not been studied much. Therefore, some experiments were performed in order to determine the synthetic potential of this rare class of heterocycles.

With a source of 2-methyleneazetidines in hand, we have briefly explored the chemistry of this system (Scheme V). Reaction of **9a** in methanol at room temperature (3 days) gave β-(arylamino) acetal **13** ($R_4$ = H). Previously, it was shown[16] that the reaction of β-chloro imines with alcohols proceeded via transient 2-alkoxyazetidines **11**, to yield β-(arylamino) acetals **13** (Scheme V). After acidic hydrolysis β-(arylamino) acetal **13** ($R_4$ = H) yielded β-(alkylamino) ketone **12** ($R_4$ = H). β-(Arylamino) ketones **12** were also prepared by reaction of 2-methyleneazetidines **9** with an aqueous sodium hydroxide solution, with an aqueous hydrogen chloride solution, or simply with water exclusively. The latter transformations proceeded via the addition of water to form 2-hydroxyazetidines, which immediately ring opened to β-(alkylamino) ketones **12**. The reaction of 2-methyleneazetidine **9b** with sodium methoxide in methanol in the presence of potassium carbonate led also to 2-methoxyazetidine **11** ($R_4$ = $CH_3$), which was already prepared by the reaction of *N*-aryl-β-chloro imines

**Scheme V**




with sodium methoxide in methanol.[16] The reaction of **9c** with methanol in the presence of potassium carbonate, which eliminates any trace of acid, leads to 2-methoxyazetidine **11** ($R_4$ = Cl). The reaction of 2-methoxyazetidine **11** ($R_4$ = $CH_3$) with lithium aluminum hydride in ether afforded azetidine **10** ($R_4$ = $CH_3$) by substitution of the methoxy group by hydride via an azetinium intermediate.

In conclusion, *N*-aryl-2-methyleneazetidines have been found to be a group of very reactive cyclic enamines prepared from β-chloro ketimines.

## Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Model 1310 spectrophotometer. $^1$H NMR spectra were measured with a Varian T-60 NMR spectrometer (60 MHz), while $^{13}$C NMR spectra were obtained with a Varian FT-80 NMR spectrometer (20 MHz). Mass spectra were recorded with a Varian Mat 112 mass spectrometer (direct inlet system or GC-MS coupling via capillary columns). Melting points were determined with a Kofler hot stage apparatus. Gas chromatographic analyses were performed with Varian 1700 and Varian 920 gas chromatographs using preparative stainless steel columns (SE 30, 3 m).

**Synthesis of β-Chloro Ketimines 7.** β-Chloro ketimines **7** were synthesized according to our previously published method involving condensation of β-chloro ketones with primary amines in ether in the presence of titanium(IV) chloride.[17]

**General Procedure for the Synthesis of 2-Methyleneazetidines 9.** To a solution of 0.01 mol of β-chloro imine **7** in 10 mL of dry *tert*-butyl alcohol was added 0.02 mol of potassium *tert*-butoxide. The stirred mixture was refluxed during several hours as indicated in Table I. Afterward the reaction mixture was cooled and 100 mL of dry pentane was added. After stirring for 1 h and filtration of the solid material, the solvent (pentane and *tert*-butyl alcohol) was evaporated in vacuo at room temperature. The residual oil was analyzed by spectroscopic means ($^1$H NMR) and/or distilled. During high-vacuum distillation partial decomposition occurred. In practically all cases, the 2-methyleneazetidines **9** thus obtained were sufficiently pure (purity >96%; GLC) for further elaboration. They have been used as such in subsequent experiments. Representative spectral data of 2-methyleneazetidines **9** are as follows.

**2-Methylene-3,3-dimethyl-1-phenylazetidine (9a, $R_1$ = H; $R_2$ = $R_3$ = Me; $R_4$ = H):** $^1$H NMR δ ($CDCl_3$) 1.28 (6 H, s, $Me_2$), 3.58 (2 H, s, $CH_2$), 4.16 and 4.84 (2 H, 2 d, AB system, $J$ = 3 Hz, $CH_2$=C), 6.50–7.50 (5 H, s, $C_6H_5$); IR (NaCl) 1667 and 1600 cm$^{-1}$; $^{13}$C NMR ($CDCl_3$) 25.5 (q, $Me_2$), 39.4 (s, $CMe_2$), 60.2 (t, $CH_2$), 74.0

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(t, $CH_2$=C), 113.1 (d, $C_{ortho}$), 128.9 (d, $C_{meta}$), 119.1 (d, $C_{para}$), 143.7 (s, $NC_{Ar}$), 159.5 (s, $CH_2$=*C*).

**6-Methyl-8-phenyl-8-azabicyclo[4.2.0]oct-1-ene (9e, $R_1R_2$ = -$(CH_2)_3$-; $R_3$ = Me; $R_4$ = H)**: $^1$H NMR δ ($C_6D_6$) 0.60–2.20 (6 H, m, $(CH_2)_3$), 1.31 (3 H, s, Me), 3.33 (2 H, s, $CH_2$), 4.93 (1 H, dd, *J* = 3.2 Hz, *J* = 4.4 Hz, C*H*=C), 6.30–7.50 (5 H, m, $C_6H_5$); $^{13}$C NMR ($C_6D_6$) 18.9, 22.2 and 31.6 (each t, 3 × $CH_2$), 23.3 (q, Me), 39.0 (s, *C*Me), 62.3 (t, $CH_2N$), 87.2 (d, *C*H=C), 113.9 (d, $C_{ortho}$), 129.1 (d, $C_{meta}$), 119.1 (d, $C_{para}$), 146.1 (s, $NC_{Ar}$), 151.3 (s, $CH_2$=*C*).

**Reactivity of 2-Methyleneazetidines 9. 1. Reaction of 2-Methyleneazetidines 9a with Methanol.** A solution of 0.01 mol of 2-methyleneazetidine **9a** in anhydrous methanol (15 mL) was stirred at room temperature during 3 days. The reaction mixture was poured into 0.5 N aqueous sodium hydroxide (100 mL) and extracted with dichloromethane (3 × 20 mL). The extracts were dried ($K_2CO_3$) for 1 h and the solvent was evaporated to leave β-(arylamino) acetal **13** ($R_4$ = H) in a pure state with 91% yield. This compound had identical spectroscopic properties as the same compound obtained via an alternative route.[16]

**2. Reaction of 2-Methyleneazetidine 9a with Methanol Followed by Reaction with Aqueous Hydrogen Chloride.** A solution of 0.01 mol of 2-methyleneazetidine **9a** in anhydrous methanol (15 mL) was stirred at room temperature during 3 days. The reaction mixture was concentrated in vacuo and afterward treated with 2 N aqueous hydrogen chloride (10 equiv). After vigorous stirring at room temperature during 2 days, the aqueous phase was made alkaline with 50% aqueous sodium hydroxide and extracted with dichloromethane (3 × 30 mL). The combined extracts were dried ($MgSO_4$) for 1 h and then the solvent was evaporated in vacuo to leave β-(arylamino) ketone **12** ($R_4$ = H) in pure state (checked by GLC and $^1$H NMR) with 87% yield. 4-(Phenylamino)-3,3-dimethyl-2-butanone (**12**, $R_4$ = H) had identical spectroscopic properties as previously described.[16]

**3. Reaction of 2-Methyleneazetidine 9a with Aqueous Sodium Hydroxide.** To 0.01 mol of 2-methyleneazetidine **9a** was added 10 molar equiv of a 2 N aqueous sodium hydroxide solution. The mixture was stirred during 1 day at room temperature and afterward extracted with dichloromethane (3 × 30 mL). The combined extracts were dried ($MgSO_4$) for 1 h, and afterward the solvent was removed in vacuo to leave β-(arylamino) ketone **12** ($R_4$ = H) in 95% yield (purity >97%; checked by GLC and $^1$H NMR).

**4. Reaction of 2-Methyleneazetidine 9b with Sodium Methoxide in Methanol and LAH Reduction.** To 0.01 mol of 2-methyleneazetidine **9b** was added 10 equiv of 2 N sodium methoxide in methanol. The reaction mixture was stirred during 10 h at room temperature, poured into water (100 mL), and extracted with dichloromethane (3 × 20 mL). The extracts were dried with potassium carbonate for 5 h and the solvent was then evaporated in vacuo. The residue containing α-methoxyazetidine **11** ($R_4$ = $CH_3$) was not totally pure (about 70–80%) and was therefore immediately treated with lithium aluminum hydride in ether. Accordingly the residue obtained as described above was diluted with 15 mL of dry ether and afterward 0.02 mol of lithium aluminum hydride in 15 mL of dry ether was added. The reaction mixture was stirred at room temperature during 3 days, then poured carefully into 200 mL of water, and extracted with dichloromethane (3 × 30 mL). The combined extracts were dried ($MgSO_4$) for 1 hour, and the solvent was removed in vacuo. The residue contained azetidine **10** ($R_4$ = $CH_3$) as the sole product, as verified by $^1$H NMR analysis and gas chromatographic analysis (purity >96%). The spectroscopic data are in agreement with data of comparable azetidines.[18]

**2,3,3-Trimethyl-1-(4-methylphenyl)azetidine (10, $R_4$ = $CH_3$)**: $^1$H NMR δ ($CDCl_3$) 1.12 (3 H, s, $CH_3$), 1.23 (3 H, s, $CH_3$), 1.31 (3 H, d, *J* = 6.4 Hz, $CH_3$CH), 2.23 (3 H, s, $CH_3C_6H_4$), 3.60 and 3.26 (2 H, 2 d, AB system, *J* = 6.4 Hz, $CH_2$), 3.65 (1 H, q, *J* = 6.4 Hz, *C*HCH$_3$), 6.50 and 7.06 (4 H, 2 d, AB system, *J* = 8 Hz, $C_6H_4$); $^{13}$C NMR δ ($CDCl_3$) 150.7 (s, *C*q), 129.0 (s, *C*q), 129.4 and 112.4 (2 d, *C*o and *C*m), 68.7 (d, *C*HCH$_3$), 64.2 (t, $CH_2$), 34.5 (s, *C*$(CH_3)_2$), 27.4 and 22.4 (2 q, $(CH_3)_2$C), 20.5 (q, *C*H$_3$), 16.8 (q, CH*C*H$_3$).

**5. Reaction of 2-Methyleneazetidine 9b with Aqueous Hydrogen Chloride.** 2-Methyleneazetidine **9b** (0.01 mol) was treated with 10 equiv of hydrogen chloride (1 N). The reaction mixture was stirred for 2 days at room temperature and then made alkaline with 50% aqueous sodium hydroxide and extracted with dichloromethane (3 × 30 mL). The combined extracts were dried ($MgSO_4$) for 1 h and the solvent was evaporated in vacuo to leave β-(arylamino) ketone **12** ($R_4$ = Me) in 95% yield; mp 61 °C (purity >96% by GLC). **4-[(4-Methylphenyl)amino]-3,3-dimethyl-2-butanone (12, $R_4$ = $CH_3$)**: $^1$H NMR δ ($CDCl_3$) 1.22 (6 H, s, C$(CH_3)_2$), 2.22 (3 H, s, $CH_3C_6H_4$), 2.18 (3 H, s, $CH_3$C=O), 3.23 (2 H, s, $CH_2$), 3.40–3.80 (1 H, s, (br), N*H*), 6.65 and 7.09 (4 H, 2 × d, AB system, *J* = 8.4 Hz, $C_6H_4$); IR (NaCl) $\nu_{C=O}$ 1709 cm$^{-1}$, $\nu_{NH}$ 3395 cm$^{-1}$; $^{13}$C NMR δ ($CDCl_3$) 213.4 (s, *C*=O), 146.2 (s, *C*q), 129.7 and 113.1 (2 × d, *C*o and *C*m), 126.6 (s, *C*p), 52.6 (t, $CH_2$), 48.7 (s, *C*$(CH_3)_2$), 25.3 (q, $CH_3$C=O), 23.0 (q, C$(CH_3)_2$), 20.3 (q, 4-$CH_3C_6H_4$), mass spectrum, *m/e* (relative intensity) 205 (11, $M^+$), 157 (7), 149 (8), 121 (9), 120 (100), 119 (5), 118 (4), 107 (12), 106 (16), 91 (14), 79 (5), 77 (7), 65 (7), 43 (10), 41 (6), 40 (22), 39 (4).

**6. Reaction of 2-Methyleneazetidine 9c with Water.** The reaction of 2-methyleneazetidine **9c** with water was performed in the same way as the reaction of 2-methyleneazetidine **9b** with aqueous hydrogen chloride, leading to 4-[(4-chlorophenyl)-amino]-3,3-dimethyl-2-butanone (**12**, $R_4$ = Cl), mp 91 °C. This compound was identical in all aspects with a compound prepared in an alternative way.[16]

**7. Reaction of 2-Methyleneazetidine 9c with Methanol and Potassium Carbonate.** The reaction of 2-methyleneazetidine **9c** with methanol in the presence of potassium carbonate was performed in the same way as the reaction of 2-methyleneazetidine **9a** with methanol, but 0.1 molar equiv of potassium carbonate was added during the reaction. 2-Methoxyazetidine **11** ($R_4$ = Cl) was isolated in 90% yield with a sufficient purity for further elaboration (>85%). **1-(4-Chlorophenyl)-2-methoxy-2,3,3-trimethylazetidine (11, $R_4$ = Cl)**: $^1$H NMR δ ($CDCl_3$) 1.13 (3 H, s, $CH_3$), 1.37 (6 H, s, 2 × $CH_3$), 3.00 and 3.26 (2 H, 2 d, AB, *J* = 6 Hz, $CH_2$), 3.37 (3 H, s, $CH_3$O), 6.57 and 7.17 (4 H, 2 d, AB, *J* = 8.2 Hz, $C_6H_4$); $^{13}$C NMR δ ($CDCl_3$) 145.6 (s, *C*q), 128.6 and 115.3 (2 d, *C*o and *C*m), 123.2 (s, *C*p), 97.4 (s, *C*$OCH_3$), 56.4 (t, $CH_2$), 51.8 (q, $OCH_3$), 41.2 (s, *C*$(CH_3)_2$), 23.2 (q, *C*H$_3$), 23.1 (q, *C*H$_3$), 15.7 (q, *C*H$_3$).

**Registry No.** **7a**, 99315-23-8; **7b**, 115437-04-2; **7c**, 115437-05-3; **7d**, 115437-06-4; **7e**, 115437-07-5; **9a**, 115437-08-6; **9b**, 115437-09-7; **9c**, 115437-10-0; **9d**, 115437-11-1; **9e**, 115437-12-2; **10** ($R_4$ = $CH_3$), 115437-15-5; **11** ($R_4$ = $CH_3$), 115461-97-7; **11** ($R_4$ = Cl), 115437-17-7; **12** ($R_4$ = H), 115437-14-4; **12** ($R_4$ = Me), 115437-16-6; **12** ($R_4$ = Cl), 85937-26-4; **13** ($R_4$ = H), 115437-13-3; $ClCH_2C(CH_3)_2COCH_3$, 13104-53-5; $PhNH_2$, 62-53-3; *p*-$MeC_6H_4NH_2$, 106-49-0; *p*-$ClC_6H_4NH_2$, 106-47-8; 1-acetyl-1-(chloromethyl)cyclohexane, 115437-03-1; 2-(chloromethyl)-2-methylcyclohexanone, 3859-32-3.

(18) Sulmon, P.; De Kimpe, N.; Schamp, N.; Tinant, B.; Declercq, J.-P. *Tetrahedron*, in press.