according to TLC analysis (9:0.4:0.8 $CHCl_3$/MeOH/NH_4OH): $[\alpha]_D$ +10.0° (c 0.26); IR (neat) 3380, 2929, 2856, 1100 cm^{-1}; ^1H NMR δ 4.21 (br s, 2 H), 4.07 (m, 1 H), 3.63 (dd, 1 H, J = 7.7, 11.2 Hz), 3.41 (dd, 2 H, J = 3.7, 11.1 Hz), 3.34 (br d, 1 H, J = 11.3), 2.09 (m, 1 H), 1.97 (m, 1 H), 1.80 (m, 1 H), 1.7–1.1 (m, 12 H); ^{13}C NMR δ 69.6 (d), 64.7 (t), 64.3 (d), 63.2 (d), 51.0 (t), 33.8 (t), 32.8 (t), 26.1 (t), 24.5 (t), 24.3 (t), 23.3 (t); MS(FI), m/z 199.

(4*S*,10*R*,11*S*)-4-(1,2-Dihydroxyethyl)quinolizidine (13b). In a manner similar to that described above for the preparation of **13a**, **13b** was obtained as a colorless oil (97%), which was pure according to TLC analysis: $[\alpha]_D$ −2.29° (c 0.7); IR (neat) 3360, 2932, 2861, 1033 cm^{-1}; ^1H NMR δ 4.09 (m, 1 H), 3.78 (dd, 1 H, J = 4.9, 10.7 Hz), 3.57 (dd, 1 H, J = 8.6, 10.7 Hz), 3.13 (br s, 2 H), 2.73 (br d, 1 H, J = 4.1 Hz), 2.58 (br d, 1 H, J = 11.5 Hz), 1.9–1.3 (m, 12 H); ^{13}C NMR δ 68.2 (t), 65.4 (d), 65.0 (d), 52.9 (d), 48.4 (t), 29.7 (t), 25.3 (t), 24.0 (t), 20.5 (t), 20.4 (t), 19.6 (t); MS(FI), m/z 199.

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A Novel Darzens-Type Condensation Using α-Chloro Ketimines

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

Jean-Paul Declercq and Bernard Tinant

Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain, 1, Place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

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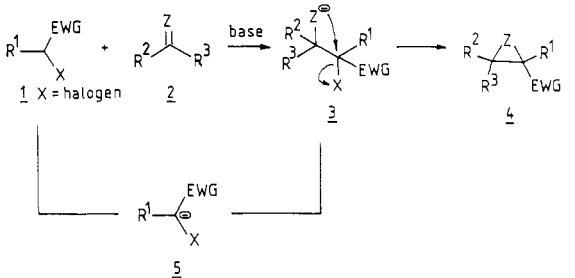
3-Chloro-1-azaallylic anions, generated by deprotonation of α-chloro ketimines with lithium diisopropylamide, reacted with ketones and aldehydes to produce 2-imidoyloxiranes (α,β-epoxy ketimines). This novel aza-Darzens-type condensation allows α-chloro ketones to condense with carbonyl compounds via protection as α-chloro ketimines. The aza-Darzens-type reaction with benzophenones as carbonyl substrate proceeded via a Favorskii-like rearrangement of an intermediate α,β-epoxy ketimine, the intermediate cyclopropylideneamine being trapped in an intramolecular way. Subsequent ring opening of the bicyclic intermediate adduct according to a so-called abnormal opening furnished rearranged 3-butenamide derivatives.

The Darzens reaction is a well-known classical reaction that enables the construction of highly functionalized oxiranes. In the most classical way,[1,2] it concerns the base-induced condensation of α-halogenated carboxylic esters **1** (EWG = COOR′) or α-halogenated nitriles **1** (EWG = CN) with carbonyl substrates **2** (Z = O) to afford α,β-epoxy esters **4** (Z = O, EWG = COOR′)[1] or 2-cyano-oxiranes **4** (Z = O, EWG = CN),[3,4] respectively (Scheme I). This reaction has been extended to various related substrates **1** such as α-halogenated sulfoxides **1** (EWG = S(O)R′),[5–10] α-halogenated sulfones (EWG = SO_2R'),[11] α-halogenated sulfoximines **1** (EWG = S(O)(=NR′)R″),[12,13] α-halogenated carboxylic amides **1** (EWG = $CONH_2$), etc. However, acyl-substituted compounds **1** (EWG = COR′), i.e. α-halogenated ketones (X = halogen), have not been condensed in Darzens-type reactions except when no α′-hydrogen atoms are present in the α-halo ketone or when special, less common substrates were used.[14] Examples of the Darzens-type reaction in the field of α-halo ketones include condensations of aromatic α-halo ketones[15] (mostly phenacyl halides)[16,17] or involve reactions of certain α-halo ketones leading to low yields of the desired acyl-substituted oxiranes.[1] A peculiar case entails an intramolecular version of the Darzens-type reaction of an aromatic α-bromo ketone.[18] The reason for the insuitability of α-halo ketones to act as substrates in Darzens-type reactions originates from their pronounced reactivity in basic medium, leading to preferred competing reactions such as the Favorskii

Scheme I



† Onderzoeksleider (Senior Research Associate) of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" (National Fund for Scientific Research), to whom correspondance should be addressed.

‡ Present address, DSM Limburg bv., Laboratory of Chemical Products, Geleen, The Netherlands.

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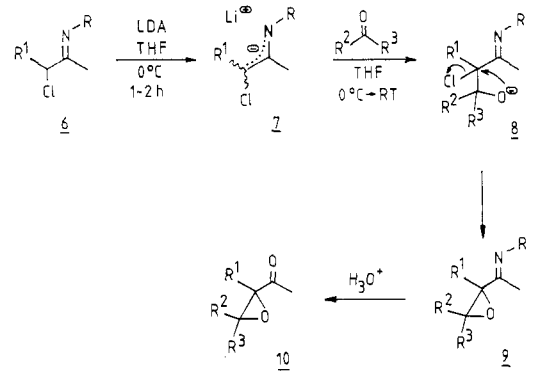
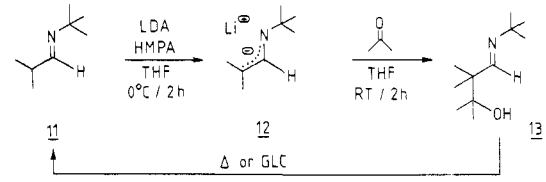
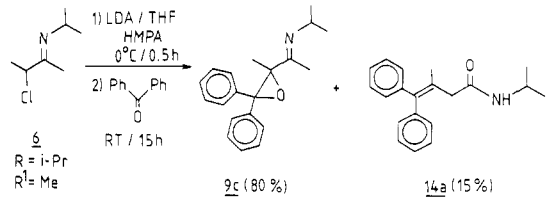
Scheme II



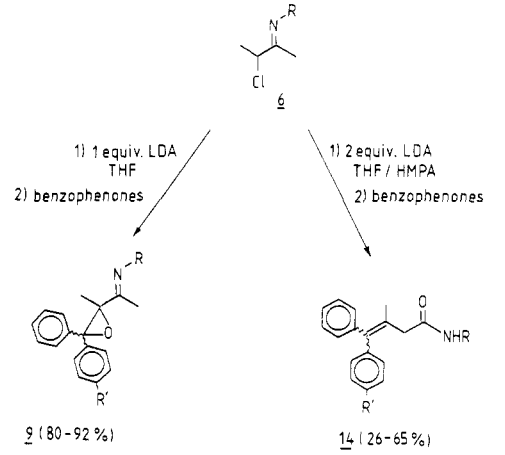
Scheme III



Scheme IV



Scheme V



rearrangement (via 1,3-dehydrohalogenation), elimination reactions (1,2-dehydrohalogenation), epoxide formation (other than the Darzens products; viz. nucleophilic addition of the nucleophilic base and subsequent intramolecular nucleophilic substitution) and nucleophilic substitution.[14] The Favorskii rearrangement is usually the pronounced reaction pathway, and this explains that phenacyl halides, which are unable to undergo 1,3-dehydrohalogenation, have been found to give Darzens-type condensations to some extent. It is also worth noting that so-called aza-Darzens reactions have been developed, namely the base-induced condensation of α-halogenated esters[19] or α-halo amides[20] with aromatic aldimines **2** (Z = NR′, R^2 = Ar, R^3 = H).

In view of our recent efforts to use α-halo imines as masked α-halocarbonyl compounds (ketones and aldehydes),[21,22] we tried to circumvent the difficulties in handling carbanions derived from α-halo ketones by using the corresponding *N*-alkyl α-halo imines. On the basis of previous results,[21] it was reasoned that α-anions derived from α-halo imines would have a good chance to react with carbonyl compounds to provide either the adducts or the ring-closed products, i.e. epoxides, resulting from a subsequent intramolecular nucleophilic substitution. Following this idea, the above mentioned reaction would entail a novel Darzens-type reaction.

Results and Discussion

α-Chloro ketimines **6**, prepared by condensation of the corresponding α-chloro ketones with a primary amine in the presence of titanium tetrachloride,[23] were converted into 1-aza-3-chloroallylic anions **7** by reaction with lithium diisopropylamide in tetrahydrofuran.[21] These regiospecifically generated heteroallylic anions **7** reacted cleanly with ketones (acetone, 2-butanone) and aldehydes (benzaldehyde) to give adducts **8**, which underwent an immediate ring closure to generate 2-imidoyloxiranes **9** (α,β-epoxy ketimines) in high yields (Table I, Scheme II). The structure of these novel functionalized oxiranes **9** was proven by spectroscopic methods (^{1}H NMR, ^{13}C NMR, IR, MS, Tables III and V) and by acidic hydrolysis to the corresponding 2-acetyloxiranes **10**.

If the same reaction sequence, involving deprotonation and reaction with the electrophile, was performed with nonchlorinated imines, e.g. aldimine **11**, the reaction with acetone led to β-hydroxyimine **13**, which could be characterized by spectroscopic methods (Scheme III). However, heating (or GLC) the β-hydroxy imine **13** resulted in a retro-aldol type cleavage to afford the starting aldimine **11** and acetone.

Any attempt to isolate the adduct from 1-aza-3-chloroallylic anion **7** and carbonyl compounds under the given reaction conditions was unsuccessful. In view of the possibility of the isolation of β-hydroxy imine **13**, it can be concluded that the conversion of **8** into oxiranes **9** is a fast intramolecular reaction.

The formation of imidoyl-substituted oxiranes **9** occurred smoothly when aliphatic ketones or benzaldehyde were used as carbonyl substrates. If the reaction of anions **7** was performed with benzophenone or substituted benzophenones, the reaction conditions needed some adaption, because a side reaction was observed during the condensation of 1-aza-3-chloroallylic anion **7** (R = *i*-Pr, R^1 = Me) with benzophenone. When 1–2 molar equiv. of lithium diisopropylamide was used for the deprotonation of α-chloro ketimine **6** (R = *i*-Pr, R^1 = Me) in the presence of HMPA, and when 2 molar equiv of benzophenone was added to the resulting anion **7**, the reaction led to 80% oxirane **9c** and 15% unsaturated amide **14a** (Table I,

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Table I. Conversion of α-Halo Ketimines 6 into α,β-Epoxy Ketimines 9

entry	R	R^1	R^2	R^3	reaction conditions[a] LDA	HMPA	R^2COR^3	yield, % 9	14	remarks
1	*i*-Pr	Me	Me	Me	1.5 E, 0 °C, 2 h		2 E, rt, 10 h	**9a**, 80		molecular distillation; bp 50–60 °C (13 mmHg)
2	*i*-Pr	Me	C_6H_5	H	1.05 E, 0 °C, 1 h	1 E	2 E, rt, 5 h	**9b**, 81[b]		compound **10** (R^1 = Me; R^2 = C_6H_5; R^3 = H) was isolated by preparative GLC after hydrolysis of the reaction mixture (sole product)
3	*i*-Pr	Me	C_6H_5	C_6H_5	1.05 E, 0 °C, 1 h		2 E, rt, 5 h	**9c**, 82		compound **10** (R^1 = Me; R^2 = R^3 = C_6H_5) was isolated by preparative GLC from the reaction mixture after hydrolysis (sole product)
4	*i*-Pr	Me	C_6H_5	C_6H_5	1.2 E, 0 °C, 1 h	1 E	1.05 E, rt, 7 h	**9c**, 80	**14a**, 15	
5	*i*-Pr	Me	C_6H_5	C_6H_5	1 E, 0 °C, 0.5 h	1 E	1 E, rt, 15 h	**9c**, 90		
6	*i*-Pr	C_6H_5	Me	Me	1.2 E, 0 °C, 1 h		2 E, rt, 15 h	**9d**, 92		
7	*i*-Pr	C_6H_5	Me	Et	1.2 E, 0 °C, 1 h		2 E, rt, 15 h	**9e**, 95		a mixture of cis and trans is formed in a ratio of 30/70 or vice versa
8	cyclohexyl	Me	C_6H_5	C_6H_5	1.2 E, 0 °C, 1 h		1 E, rt, 15 h	**9f**, 92		

[a] E = molar equivalents; rt = room temperature. [b] Yield of the reaction mixture. Immediate hydrolysis to the corresponding α,β-epoxy ketone **10** (R^1 = Me; R^2 = C_6H_5; R^3 = H) was performed.

Table II. Synthesis of 3-Butenamides 14

entry	R	R′	reaction conditions[a] LDA[a]	HMPA	benzophenone	yield, %	mp, °C
1	*i*-Pr	H	2 E, 0 °C, 0.5 h	1 E	1 E, 0 °C, 5 h	**14a**, 26	134
2	*i*-Pr	H	2 E, 0 °C, 0.5 h	1.2 E	1 E, 0 °C, 5 h	**14a**, 43	134
3	*i*-Pr	H	2 E, 0 °C, 1 h	2 E	1 E, 0 °C, 5 h	**14a**, 52	134
4	*t*-Bu	H	2 E, 0 °C, 1 h	2 E	1 E, 0 °C–rt, o.n.	**14b**, 65	108
5	*t*-Bu	Cl	2 E, 0 °C, 1 h	2 E	1 E, 0 °C–rt, o.n.	**14c**, 45[b]	70
6	cyclohexyl	H	2 E, 0 °C, 1 h	2 E	2 E, 0 °C, 7 h	**14d**, 53	151

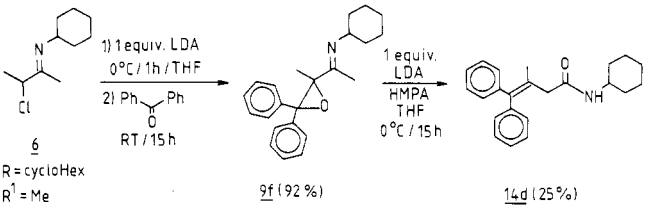
[a] E = molar equivalents; rt = room temperature; o.n. = overnight period. [b] A 50:50 mixture of cis and trans was observed.

Scheme IV). These rearranged amides, such as **14a**, were only formed when benzophenones were used as the electrophiles. Adaption of the reaction conditions toward the use of 1 molar equiv of lithium diisopropylamide resulted in the formation of oxirane **9c** (and other analogues), exclusively. When 2 molar equiv of lithium diisopropylamide was used during the deprotonation of α-chloro ketimines **6** and subsequent reaction with benzophenones, the reaction gave rise to the unsaturated amides **14** in 26–65% yield (Table II, Scheme V). It is worth noting that the synthesis of 3-butenamides **14** occurred only to appreciable yields if hexamethylphosphorus triamide (HMPA) was present in the medium.

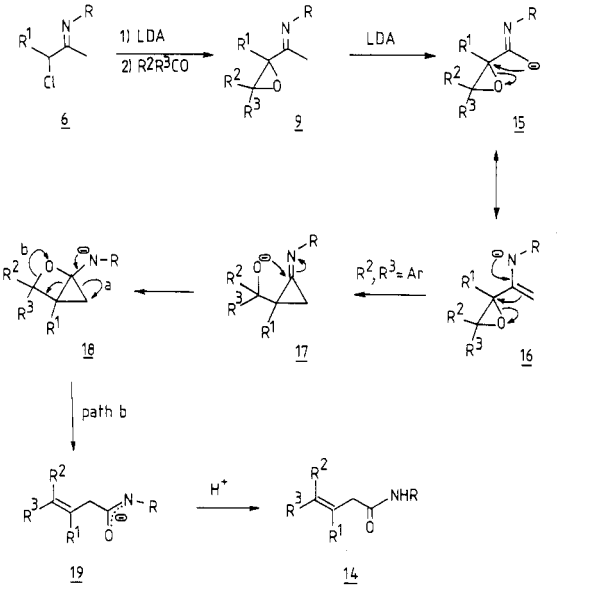
It was proven that geminal diphenyloxiranes **9** were the intermediates in the formation of 3-butenamides **14**. Oxirane **9** (R = cyclohexyl, R^1 = Me, R^2 = R^3 = Ph), prepared in 92% yield by reaction of *N*-cyclohexyl-α-chloro ketimine **6** (R = cyclohexyl, R^1 = Me) with 1 molar equiv of lithium diisopropylamide and benzophenone, was treated with 1 molar equiv of lithium diisopropylamide and 1.2 molar equiv of hexamethylphosphorus triamide in tetrahydrofuran during 15 h at 0 °C. This conversion of oxirane **9f** with LDA afforded 3-butenamide **14d** in 25% as the sole isolable product, indicating the intermediacy of oxiranes **9** in the transformation of α-chloro ketimines **6** into amides **14** (Scheme VI).

On the basis of the preceding results, the formation of 3-butenamides **14** from α-chloro ketimines **6** is explained in the following way (Scheme VII). α-Chloro ketimines **6** were deprotonated with LDA and reacted with benzophenone to afford geminal diphenyloxiranes **9**. These oxiranes **9** were stable toward an excess of the base (LDA) except for the more reactive geminal diaryl derivatives **9** (R^2, R^3 = Ar). Oxiranes **9** are α-functionalized imines with the intrinsic value of a leaving group in the α-position. Base-induced intramolecular cleavage of the oxirane ring

Scheme VI

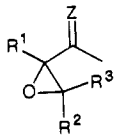


Scheme VII



by attack of the α′-anion is a negligible process for the alkyl-substituted oxiranes **9** (R^2, R^3 = alkyl) but becomes an important pathway for the activated diaryl derivatives

Table III. Spectral Data (IR, ^{1}H NMR, MS) of Functionalized Oxiranes 9 and 10[a]

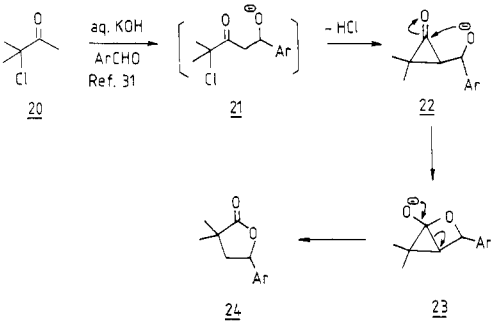


	Z	R^1	R^2	R^3	IR (NaCl, cm^{-1}) $\nu_{C=N}$, $\nu_{C=O}$	^{1}H NMR (δ, $CDCl_3$)	mass spectrum (70 eV), m/e (%)[b]
10a	O	Me	C_6H_5	H	1712	1.20 (3 H, s, CH_3CO), 2.17 (3 H, s, $CH_3C{=}O$), 4.18 (1 H, s, CH), 7.30 (5 H, s, C_6H_5)	
10b	O	Me	C_6H_5	C_6H_5	1715	1.34 (3 H, s, CH_3CO), 1.72 (3 H, s, $CH_3C{=}O$), 7.00–7.80 (10 H, m, $(C_6H_5)_2C$)	252 (M^+, 9), 165 (100), 105 (46), 77 (44)
9a (*E*/*Z*)	*N*-*i*-Pr	Me	Me	Me	1665	1.08 and 1.12 (6 H, 2 d, J = 6 Hz, $CH(CH_3)_2$), 1.37 (3 H, s, CH_3), 1.45 (3 H, s, CH_3), 1.87 and 2.01 (3 H, 2 s, $CH_3C{=}N$ (*E*/*Z*)), 1.19 (3 H, s, CH_3), 3.73 (1 H, s, $CH(CH_3)_2$)	169 (M^+, 4), 84 (26), 43 (20), 42 (100)
9c	*N*-*i*-Pr	Me	C_6H_5	C_6H_5	1665	0.92 and 1.01 (6 H, 2 d, J = 6.2 Hz, $CH(CH_3)_2$), 1.34 and 1.48 (6 H, 2 s, $CH_3C{=}N$ and $CH_3CC{=}N$), 3.45 (1 H, septet, J = 6, 2 Hz, $CH(CH_3)_2$), 7.00–8.00 (10 H, m, $(C_6H_5)_2$)	
9d	*N*-*i*-Pr	C_6H_5	Me	Me	1668	1.03 (3 H, s, CH_3), 1.17 (6 H, d, J = 6.2 Hz, $(CH_3)_2CH$), 1.40 (3 H, s, CH_3), 1.82 (3 H, s, $CH_3C{=}N$), 3.73 (1 H, septet, J = 6.2 Hz, $CH(CH_3)_2$), 7.10–7.80 (5 H, s, C_6H_5)	231 (M^+, 2), 84 (37), 43 (89), 42 (100)
9e	*N*-*i*-Pr	C_6H_5	Me	Et	1665	0.80–2.00 (14 H, m, $CH(CH_3)_2$, CH_3, and CH_3CH_2 (c/t)), 1.79 (3 H, s, $CH_3{=}N$), 3.70 (1 H, septet, J = 6.2 Hz, $CH(CH_3)_2$), 7.10–7.80 (5 H, m, C_6H_5)	(cis)[c] 245 (M^+, 7), 84 (75), 43 (19), 42 (100); (trans)[c] 245 (M^+, 4), 105 (19), 84 (77), 42 (100)
9f	*N*-cyclohexyl	Me	C_6H_5	C_6H_5	1660	1.36 (3 H, s, CH_3), 1.45 (3 H, s, CH_3), 0.9–2.2 (10 H, m, C_6H_{10}), 2.6–3.4 (1 H, m, NCH), 7.0–8.0 (10 H, m, $(C_6H_5)_2C$)	333 (M^+, 1), 182 (40), 105 (100), 77 (65)

[a] Compounds **9** gave correct elemental analyses. [b] Only the molecular ion (M^+) and the three most abundant fragmentations are given. [c] Or vice versa.

9 (R^2, R^3 = aryl). Base-induced 1,3-interaction of α-functionalized ketones is well-known as a step in the Favorskii rearrangement[24] of α-halo ketones (the halogen being the leaving group). More recently, α-halo imines were also shown to afford the Favorskii rearrangement with bases.[25-27] Analogously, considering the α,β-epoxy moiety of 2-imidoyloxiranes **9** as a potential leaving group (C_α–O cleavage) of the α-position opens the possibility of a 1,3-displacement upon deprotonation at the α'-position (see anion **15**). The leaving group character of the epoxide is substantially increased by the geminal diaryl substitution and enables the conversion of anion **15** into the intermediate cyclopropylideneamine **17** to take place according to a Favorskii-like rearrangement. The Favorskii rearrangement was recently shown to proceed via cyclopropylideneamines,[26,27] i.e. N-analogues of the well-known cyclopropanones. Thus, the ring contraction of carbanion **15** into cyclopropylideneamine derivative **17** is most probably a part of the first Favorskii-like rearrangement of an α,β-epoxy ketimine **9**. This transformation is a plausible conversion because some examples of the base-induced Favorskii-rearrangement of α,β-epoxy ketones are known in the literature.[28-30] It is clear from the structure

Scheme VIII



of the intermediate cyclopropylideneamine **17** that this compound will not survive as such but will undergo an intramolecular nucleophilic addition of the alkoxide across the reactive carbon–nitrogen double bond to afford bicyclic intermediate **18**. A similar bicyclic intermediate **23** was recently proposed to explain the rearrangement of α-chloro ketone **20** with aqueous potassium hydroxide in the presence of aromatic aldehydes to yield γ-lactones **24** (Scheme VIII).[31] Favorskii intermediates, i.e. adducts of cyclopropanones or cyclopropylideneamines, open in such a way as to produce the most stable carbanion, which further leads to the final rearranged products.[24,26] Ring opening of bicyclic adduct **18** according to "route a" produces a primary carbanion, which is more stable than the carbanion derived from opening via "route b". However, the so-called "abnormal" ring opening via path b enables cleavage of the strained oxetane structure with expulsion

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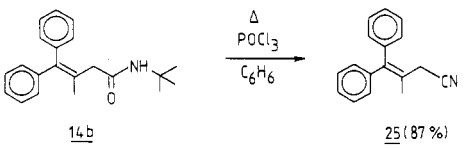
Table IV. Spectral Data (IR, ^{1}H NMR, MS) of 3-Butenamides 14 and Nitrile 25[a]

	R	R′	IR (KBr, cm^{-1}) $\nu_{C=O}$	IR (KBr, cm^{-1}) ν_{NH}	^{1}H NMR (δ, $CDCl_3$)	mass spectrum (70 eV), m/e (%)[b]
14a	*i*-Pr	H	1641	3320	1.14 (6 H, d, J = 6.2 Hz, $CH(CH_3)_2$), 1.90 (3 H, s, CH_3C=), 3.03 (2 H, s, CH_2), 3.80–4.40 (1 H, m, $CH(CH_3)_2$), 5.35 (1 H, s, br, NH), 7.27 (10 H, s, $(C_6H_5)_2C$)	293 (M^+, 81), 208 (100), 129 (62), 91 (56)
14b	*t*-Bu	H	1646	3340	1.32 (9 H, s, $(CH_3)_3C$), 1.87 (3 H, s, CH_3C=), 2.97 (2 H, s, CH_2), 5.30 (1 H, s, br, NH), 7.22 (10 H, s, $(C_6H_5)_2C$)	307 (M^+, 23), 208 (75), 105 (100), 57 (88)
14c[c]	*t*-Bu	Cl	1642	3305	1.34 and 1.36 (9 H, s, $(CH_3)_3C$ (c/t)), 1.86 and 1.88 (3 H, s, CH_3=C (c/t)), 2.97 (2 H, s, CH_2), 5.27 (1 H, s, br, NH), 7.00–7.50 (9 H, m, C_6H_5 and C_6H_4)	no M^+, 69 (53), 67 (57), 55 (100)
14d	cyclohexyl	H	1635	3322	0.60–2.20 (10 H, m, $(C_6H_5)_2C$), 1.88 (3 H, s, CH_3C=), 3.03 (2 H, s, CH_2), 3.30–4.10 (1 H, m, NHCH), 5.20–5.60 (1 H, m, NH), 7.23 (10 H, s, $(C_6H_5)_2C$)	333 (M^+, 1), 182 (33), 105 (100), 77 (60)
25				2263 ($\nu_{C\equiv N}$)	1.94 (3 H, s, CH_3C=), 3.13 (2 H, s, CH_2), 7.23 (10 H, s, $(C_6H_5)_2C$)	233 (M^+, 100), 232 (23), 191 (23), 165 (23), 115 (23)

[a] Compounds 14 gave correct elemental analyses. [b] Only the molecular ion (M^+) and the three most abundant fragmentations are given. [c] 50:50 mixture of cis and trans isomers.

Scheme IX



14b 25 (87%)

of an oxygen anion, the charge of which is delocalized over the amide functionality of **19**. On aqueous workup, the anion **19** is transferred into the final β,γ-unsaturated amide **14**.

The structure of the β,γ-unsaturated amides **14** was established by spectroscopic methods (Tables IV and VI) and by chemical transformation. The structural proof for an amide functionality in compounds **14** was obtained from the reaction of the *N-tert*-butyl amide **14b** (R = *t*-Bu; $R^2 = R^3 = C_6H_5$) with phosphorus oxychloride in benzene (von Braun reaction).[32] After 7 h of reflux, the nitrile **25** was produced in 87% yield, but 10% unreacted amide **14b** was still present in the reaction mixture (Scheme IX). Finally, the structure of the rearranged amides **14** was definitively proven by X-ray crystallographic analysis of *N*-isopropyl-3-methyl-4,4-diphenyl-3-butenamide (**14a**) (*R* = *i*-Pr; $R^2 = R^3 = C_6H_5$). Figure 1 displays the spatial arrangements of the various atoms in amide **14a**.

All 3-butenamides **14** and 3-butenenitrile **25** are new compounds. Some related structural analogues are known in the literature. For instance, *N*-alkyl-4,4-diphenylamides were already prepared from the corresponding carboxylic acid chlorides on reaction with primary amines,[33-41] while 2-methyl-3-phenyl-2-propenenitrile and 3,3-diphenyl-2-propenenitrile were obtained from the reaction of the appropriately substituted allyl chloride with cyanide.[42-46]

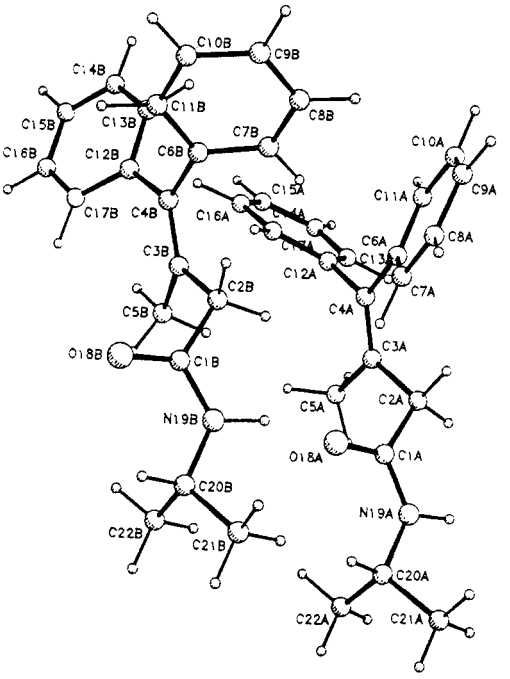


Figure 1. X-ray crystallographic analysis of *N*-isopropyl-3-methyl-4,4-diphenyl-3-butenamide (**14a**).

In conclusion, the Darzens-type condensation of α-halo ketones, previously being limited to special cases, has been made possible via α-halo imines, i.e. masked α-halo ketones, to provide 2-imidoyloxiranes. These α,β-epoxy ketimines can be hydrolyzed into the corresponding α,β-epoxy ketones, indicating a route for executing Darzens reactions with α-halo ketones. This reaction is complementary to the classical epoxidation of enones with hydrogen peroxide in alkaline medium.[47] Reference should be made to a related condensation of a functionalized 2-(1-bromoethyl)-2-oxazoline, i.e. an α-brominated cyclic imino ether, with acetone under the influence of LDA to yield the aldol-type adduct, which did not cyclize to the

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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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