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Journal

Australian Journal of Chemistry, 63(12)

ISSN

0004-9425

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Publication Date

2010-12-20

DOI

10.1071/CH10318

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New Syntheses and Ring Expansion Reactions of Cyclobutenimines

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Two routes are reported for the synthesis of iminocyclobutenones having *N*-(het)aryl substitution: an addition/substitution sequence starting with cyclobutenediones and an aza-Wittig method. A new synthetic route to *N*-alkyl derivatives is also presented. This involves *O*-alkylation of 3-alkylamino-1,2-cyclobutenediones using Meerwein's reagent and subsequent deprotonation under non-hydrolytic conditions. Lithium organyls were found to add to the remaining carbonyl group. The resulting tertiary alcohols undergo ring enlargement on heating in xylene to give 4-aminophenols, 4-amino-1-naphthols, or cyclopenta-annulated quinolines from 4-vinyl, 4-aryl, and 4-alkynyl derivatives, respectively.

Manuscript received: 30 August 2010.

Manuscript accepted: 1 November 2010.

Introduction

Cyclobutenones **1**, containing an enone unit in a four-membered ring, combine ring strain with the well known enone reactivity.^[1] Syntheses of these highly substituted derivatives are available, and these undergo facile electrocyclic ring opening to give conjugated ketene intermediates. Subsequent ring closures provide useful synthetic routes to numerous other

compounds.^[2–4] Moreover, the cyclobutenone unit is found in important derivatives such as cyclobutene-1,2-diones **2**,^[4–7] semisquaric acid **3**,^[8] squaric acid **4**,^[6,9] and its aromatic squarate **5** dianion (Scheme 1).^[9,10]

Much less is known about heteroanalogues of cyclobutenones. Selected examples include monothiolation of semisquaric **3** to give the corresponding 4-thioxocyclobut-2-enones.^[11] Also 1,3-dithiolane derivatives of cyclobutenones have been synthesized,^[12,13] which can be considered as protected cyclobutenethiones.^[14–16] There are also scattered examples of cyclobutenimine derivatives in the literature. For example, cyclobuta[e]triazines **6** and cyclobuta[c]quinoxalinones **7** were obtained when cyclobutenediones **2** were treated with the corresponding nitrogen biselectrophiles such as amidrazones^[17–19] or 1,2-diaminobenzenes, respectively.^[18–21] Semisquaric acid derivatives yield cyclobutenone hydrazones **8** upon treatment with arylhydrazones^[19] and cyclobutenone oximes

Scheme 1. Cyclobutenone structures.

Scheme 2. Compounds with a cyclobutenimine unit.

are available by aza-Wittig monoimination of cyclobutenediones.^[22] The reaction of squaric or semisquaric acid derivatives with aromatic amines gives zwitterionic compounds,^[9,23,24] e.g., **9**^[23] (Scheme 2). Cyclobutenimmonium structures were also obtained by [2+2] cycloaddition of ynamines and the related α -chloroenamines to give chlorides **10**^[25,26] or by alkylation of squaric acid amides to give products **11** (Scheme 2).^[9,27] In another approach, cyclopropanones^[28–31] or their all-carbon analogues, triafulvenes, react with isonitriles to give cyclobutenimines of type **12** and **13**, respectively (Scheme 2).^[32]

Recently, the conversion of 2,2,4,4-tetrachlorocyclobutanamines **14** to cyclobutenimine acetals **15** by the action of alkoxide in a mixed elimination/substitution process was reported (Scheme 3).^[33]

Comprehensive studies of cyclobutenimine chemistry demanded a more general synthesis since the above methods

Scheme 3. Cyclobutenimines from tetrachlorocyclobutanamines.

Scheme 4. Synthesis of dialkyl squarates.

suffer a lack of synthetic scope. 4-Iminocyclobutenones were particularly attractive goals since the remaining carbonyl group provides a site for subsequent synthetic manipulation. Progress towards developing general routes to such compounds is now outlined below.

Synthesis of 4-Iminocyclobutenones

A particularly convenient route to cyclobutenones and cyclobutenediones employs squaric acid **4** as the basic starting material. This is esterified to give squarates **16** via azeotropic removal of water or by the action of the corresponding orthoformate (Scheme 4). For a multigram synthesis of the methyl ester (**16**, $\text{R}^1 = \text{Me}$), the orthoester route is most convenient.^[34] However, for the present work we mainly used diisopropyl squarate (**16**, $\text{R}^1 = i\text{Pr}$),^[35] which was easily obtained as a crystalline white solid by the azeotropic esterification method (Scheme 4). Diisopropyl squarate has advantages over other analogues. For example, it is less easily hydrolyzed than the dimethyl derivative and is safer to use since the dimethyl analogue was shown to be a potent skin allergen.^[36,37]

Scheme 7. Aza-Wittig synthesis of 4-iminocyclobutenones.

Scheme 5. Squarate modification by an addition/substitution approach.

Scheme 6. The organyl addition/substitution route to cyclobutenimines.

The alkoxy groups in **16** can be replaced by alkyl, alkenyl, or aryl groups by the action of the corresponding lithium organyl. For example, treatment of the squarate with an organometallic reagent followed by the addition of trifluoroacetic anhydride gave the trifluoroacetate **17** which was not isolated but treated directly with oxygen nucleophiles. Thus, treatment of **17** with water gave 4-substituted cyclobutenediones (semisquarates) **18** and with alcohols the corresponding acetals **19** were realized (Scheme 5).^[38,39] This method also allowed use of silyl anions as nucleophiles to give silyl-substituted cyclobutenones **18**, **19**.^[40]

Cyclobutenediones **19** may be submitted to the above reaction sequence to give 3,4-disubstituted-1,2-cyclobutenediones **2**.^[38]

In still another variant, dimethyl squarate **16** ($R^1 = \text{Me}$) was treated with methyl lithium (2.5 equivalents) thus introducing two methyl groups simultaneously to give 3,4-dimethylcyclobut-3-ene-1,2-dione **2** ($R^1 = R^2 = \text{Me}$) in excellent yield (95%).^[41]

The efficient reaction of intermediate **17** with oxygen nucleophiles (Scheme 5) suggested that **17** might be analogously trapped by amines to give iminocyclobutenones.^[42] In fact, trifluoroacetate **17**, formed from ester **16** and an (het)aryl lithium compound (Scheme 5), reacted smoothly with various anilines or 3-aminopyridine to yield the *O,N*-acetals **20**. These then undergo spontaneous elimination of 2-propanol to give the desired compounds **21** in good to excellent yields (Scheme 6).

Scheme 8. Attempted synthesis of *N*-silylcyclobutenimines.

Scheme 9. Synthesis of 4-(alkylimino)cyclobutenones.

Scheme 10. Hydroquinones by ring expansion of 4-alkenylcyclobutenones.

The structure assignments of **21** are based upon both spectral and chemical data. For example, the IR spectra of **21** show imino stretch vibrations around 1690 cm^{-1} and carbonyl stretch vibrations at 1750 cm^{-1} . Their ^{13}C NMR spectra reveal resonances

Scheme 11. Light-induced electrocyclic ring opening of cyclobutenimines.

for the imino and carbonyl carbons at approximately $\delta = 165$ and 188 , respectively. Interestingly, in each case only one set of NMR signals was observed even though inversion at the imino nitrogen should be slow on the NMR time scale.^[43] This indicates that only one diastereomer is formed.

N-(Het)arylcyclobutenimines **21** are reasonably stable and can be purified by chromatographic methods. Such stability is consistent with previous reports showing that imine hydrolysis of *N*-arylcyclobutenimines required heating with 2 M hydrochloric acid.^[33] Attempts to expand the scope of the method for the synthesis of *N*-alkyl-iminocyclobutenones resulted in the isolation of the corresponding cyclobutenediones **2**. Apparently, unlike their *N*-(het)aryl counterparts, *N*-alkyl derivatives readily hydrolyze during workup to give **2**. The only exception was the

Scheme 12. Reaction of 2-phenyl-3-isopropoxy-4-iminocyclobutenones and of 3-phenyl-4-isopropoxy-1,2-cyclobutenediones with 1-alkenyl lithium compounds.^[42]

Scheme 13. Ring expansion of 4-alkenylcyclobutenimines.^[42]

Scheme 14. Synthesis and ring expansion of 4-arylcyclobutenimines.^[42]

N-tert-butyl derivative **21** (Ar = Ph, R = *t*Bu), which was isolated in 72% yield.

An alternative method for the synthesis of *N*-arylimino-cyclobutenones **21** was developed and is outlined as follows.^[42] It is well established that the reaction of iminophosphoranes with carbonyl compounds constitutes an excellent method for the construction of imino groups ('aza-Wittig' reaction).^[44,45] To test this in the cyclobutenone series, **18** (R¹ = *i*Pr; R² = Ph) was treated with (*N*-phenylimino)triphenylphosphorane and this gave the corresponding **21** in 89% yield. This compound was identical to the iminocyclobutenone obtained in 73% by the method outlined in Scheme 6. As expected, the enone carbonyl rather than the vinylogous ester in **18** reacts preferentially with the aza-Wittig reagent. It is noteworthy that *N*-(2- or 4-pyridyl) derivatives could be obtained by this method (Scheme 7) but not by the route outlined in Scheme 6.

In attempts to expand the synthetic scope of the aza-Wittig method, 3-alkoxy-4-phenyl-1,2-cyclobutenediones **18** were treated with *N*-(trimethylsilyl)imino-triphenylphosphorane. Surprisingly, the corresponding 4-(trimethylsilylimino)cyclobutenone **21** was not found (Scheme 8). Instead, the unusual bicyclic product **24** was isolated (Scheme 8).^[46] The tentative structure assignment is based on spectral and analytical data. That is, the IR spectrum shows absorptions for the strained carbonyl and imine at 1758 and 1721 cm⁻¹, respectively, which may seem reasonable when compared with absorptions at 1760

and 1670 cm⁻¹ for the analogous unit in **7** (Scheme 2) and in the light of imine absorptions in *N*-phosphinyl imines in the 1680–1690 cm⁻¹ range,^[47] i.e. at higher wavenumber than ordinary imines (1610–1635 cm⁻¹).^[48] The ¹³C NMR spectrum shows low-field resonances at δ = 200.5, 200.4, 195.7, and 191.7. Formation of **24** is assumed to involve initial attack of the iminophosphorane on the more reactive carbonyl group of **18** to give **22**. This zwitterionic intermediate, having a choice of an aza-Wittig^[44,45] or aza-Peterson reaction,^[49,50] eliminates trimethylsiloxide followed by dealkylation to give **24**.

The synthesis of iminophosphoranes as outlined here requires potentially dangerous organic azides which are often not readily available. Also, the aza-Wittig route to **21** (Scheme 7) does not allow access to *N*-alkylimino derivatives. These shortcomings were overcome by employing semisquaric acid amides **25**, which are readily obtained from the corresponding semisquarates **18**.^[9,11,24,51,52] Specifically, *O*-alkylation of **25** using Meerwein reagent in refluxing dichloromethane generated cyclobutenimmonium salts **26**, which were unstable when exposed to moist air and regenerated the starting amides **25**. However, they can be deprotonated under non-hydrolytic conditions using a bulky base with proton sponge (1,8-bis-dimethyl-amino-naphthalene)^[53] at room temperature giving the best results (Scheme 9). Precipitation of the salt is enhanced by cooling to -10°C. The spectroscopic data of the *N*-alkyl derivatives resemble those of the *N*-aryl compounds **21**, i.e. they show a carbonyl stretch in their IR spectra at 1756 cm⁻¹ and a vinylogous imide stretch at 1699 cm⁻¹. In analogy to the *N*-aryl derivatives, their NMR spectra show only one set of signals implying again a fixed configuration of the imino unit.^[46]

Scheme 15. Synthesis and ring expansion of 4-arylcyclobutenones.^[42]

Ring Expansion Chemistry of Cyclobutenimines

Significant synthetic utility of cyclobutenones **1** rests on their thermally induced 4 π -electrocyclic ring opening to reactive alkenylketene^[3] intermediates coupled with the subsequent 6 π -electrocyclic ring closure involving appended unsaturated side chains to give ring expanded products.^[2,4,54] For example, a unique synthesis of hydroquinones involves the thermolysis of 4-alkenylcyclobutenones to give initially dienylketenes, which provide the hydroquinones upon 6 π -electrocyclic ring closure (Scheme 10).

Scheme 16. Synthesis and ring expansion of 4-alkynylcyclobutenimines.

Scheme 17. Alternate reaction pathways in the cyclization of ketenimine **42**.^[42]

Scheme 18. Synthesis and ring expansion of 4-alkynyl-*N*-pyridyl-cyclobutenimines.^[42]

Although it was an open question whether cyclobutenimines would behave analogously, anticipation of such was suggested based upon previous work showing that photolysis of an iminocyclobutenone of type **21** leads to products apparently derived from an α,β -unsaturated alkenyl ketenimine derivative (Scheme 11).^[28,29,55]

The availability of iminocyclobutenone **21** as outlined above allowed a study of their reactions with lithium organyls in anticipation of establishing a viable route to the required cyclobutenimines having unsaturated substituents at position-4. Thus, iminocyclobutenones **21** were treated with vinyl lithium or 2-propenyl lithium giving good to excellent yields of the 1,2-adducts **27** (Scheme 12). The IR spectra of these adducts lack the presence of a carbonyl absorption but do show the presence of an imino absorption at approximately 1690 cm^{-1} . Similarly, their ^{13}C NMR spectra show no carbonyl resonance, but they do show the absorption for the imino carbon at approximately δ 165. Chemical evidence for their assigned structures rests on their observed acid-catalyzed hydrolysis to give the vinylogous hemiacetal **28** (Scheme 12).^[42]

In passing it is noted that **28** and **29** are regioisomeric, the former arising from the iminocyclobutenone **21** and the latter from cyclobutendione **18**. As a result, **21** is effectively a protected form of **18** and together these provide a potentially useful route to regioisomeric cyclobutenones. This aspect has

been exploited in natural product synthesis by the Moore^[56] and Trost^[57] groups to secure the required regiochemistry in the target compounds.

Iminocyclobutenes **27** are stable at room temperature, but upon heating undergo ring expansion to give the aminophenols **31** (Scheme 13). This transformation apparently involves electrocyclic ring opening of **27** to the corresponding dienylketenimine intermediates **30** followed by ring closure to ultimately give the observed products. Thus, these iminocyclobutenes follow the same general reaction pathway as that previously reported for the analogous cyclobutenones (Scheme 10).

Once again, since **28** and **29** are regioisomers, their synthesis and the above ring expansion provides selective control of the substitution pattern of the corresponding aminophenols. Furthermore, since the aminophenols are precursors to the corresponding quinones upon oxidation with silver(I) oxide,^[58] they can also control the quinone substitution pattern.

Following the successful synthesis and ring expansion of 4-(1-alkenyl)-cyclobutenimines **27**, our study was then extended to include the synthesis and ring expansion of 4-aryl analogues (Scheme 14). Again regioselective 1,2-addition to the carbonyl group in **27** is observed to give **33** when the intermediate alkoxide was quenched with water ($R^2 = \text{H}$) or methyl triflate ($R^2 = \text{OSO}_2\text{CF}_3$). By analogy to the ring expansion of 4-(1-alkenyl) derivatives **27** (Scheme 13), heating **33** in xylene

Scheme 19. Synthesis and ring expansion of a 4-alkynyl-4-trimethylsiloxy-cyclobutenimine.

Scheme 20. Synthesis and ring expansion of a 4-alkynyl-*N*-mesitylcyclobutenimine.^[42]

provides aminonaphthols or naphthyl ethers (Scheme 14). The naphthols tend to be oxidized by air while the ethers are reasonably stable compounds. The two products **35**, **36** arise from the iminoketene **34** bearing a *m*-substituted aryl group ($R^1 \neq H$). Thus two possible ring closure pathways are available. Here, the position *para* to substituent R^1 is sterically less shielded and may also be electronically preferred, thus influencing the preference for product **35**. The same competition of two substitution pathways was observed earlier for the cyclization of the ketene congeners **37** of ketenimines **34**, in which the cyclization to **39/40** was found to be less selective, demonstrating the higher electrophilicity and thus lower selectivity for ketene **38** attack as compared with attack by the ketenimine **34** (Scheme 15).^[59] Also the smaller carbonyl group in ketenes relative to the imino unit in ketenimines may further reduce selectivity.

Analogously to their alkenyl and aryl congeners, alkynyl lithium reagents were found to react with 4-iminocyclobutenones **21** to give 4-alkynylcyclobutenimines **41** by 1,2-addition (Scheme 16).^[42] Thermolysis of these did not result in facile ring expansion to iminoquinones (Scheme 14) as did the corresponding 4-alkenylcyclobutenone ring expansion to quinones (see Scheme 15). Low yields of these were realized (Scheme 17) but the major product was the cyclopentannulated quinolines **45**, isolated in 10–49% yield.^[42] In analogy to the 4-alkynylcyclobutenone series,^[60,61] the diradical **43** is presumably involved which allows delocalization of an unpaired electron into the *N*-aryl substituent. Diradical ring

closure at an *o*-position of the *N*-phenyl substituent occurs. The moderate to low yields may be due to the fact that an oxidation step from the primary product **44** to **45** is involved, but the nature of the oxidant is not known. It might be oxygen from air during workup, but a possible oxidizing agent might also be an iminoquinone **47**, which in some cases was isolated in low yield (~20%) from the complex reaction mixture along with the aminophenol **48** (~18%). Products **47**, **48** are presumably formed from the enynylketenimine **42** via radical attack at the terminal alkyne carbon (Scheme 17), a transformation in analogy to the cyclobutenone/quinone reaction (Scheme 10).

The interesting heterocycles formed on heating the *N*-(3-pyridyl)- and the *N*-(4-pyridyl)-cyclobutenimines **21** appear to stem from the same pathway as the 4-aryl derivatives (Scheme 18), i.e. **50/51** and **52** respectively. Two cyclization modes are possible starting from **21** ($R^2 = 3$ -pyridyl) and, in fact, two products **50** and **51** are isolated (Scheme 17, upper reaction). Structure assignment is based on analogy and on the spectroscopic data. Specifically, a characteristic feature of **50** is a broad singlet in the 1H NMR spectrum at δ 9.44 for H-9 (Scheme 17). This proton gives resonance at δ 9.00 in product **52**.^[42]

Further mechanistic insight for the 4-alkynylcyclobutenimine rearrangements was obtained from a study of the thermolysis of 4-alkynyl-4-trimethylsiloxy-cyclobutenimine **53**. Here, the product was the quinoline **55**, isolated in 19% yield (Scheme 19). Thus, the trimethylsiloxy group in **51** prevents facile oxidation as was noted for **44** giving further evidence for

the mechanistic details outlined above. Evidence for the suggested structure of **55** comes from its ^1H NMR spectrum showing the cyclopentyl methine hydrogen at δ 5.53 and from NOE experiments where irradiation of the cyclopentyl methine resonance caused a 7% enhancement of the absorption of the methine hydrogen of the isopropoxy group at δ 4.29. Likewise, irradiation of the absorption at δ 4.29 caused a 10% enhancement of the cyclopentyl hydrogen absorption at δ 5.53.^[42]

A prerequisite for the formation of products **45** and **55** is the presence of an unsubstituted *o*-position in the *N*-phenyl substituent. Therefore, a methyl group in this position should prevent ring closure on the *N*-aryl group. This was, in fact, observed. Specifically, thermolysis of the *N*-mesityl derivative **56** in refluxing xylene gave the cyclopentene **57** in 53% isolated yield (Scheme 20). The formation of **57** is assumed to arise via hydrogen abstraction from the proximal hydroxy group in a diradical intermediate analogous to **43**. The structure **57** was proven by a single-crystal X-ray investigation.^[42] It should be noted that the observed *E* configuration of the exocyclic C=C unit in **57** speaks against an intramolecular hydrogen transfer from the hydroxy group in **43**.

Conclusions

Three routes to 4-iminocyclobutenones **21** were developed. In all cases, lithium organyls bearing unsaturated organic residues undergo selective 1,2-addition to the enone carbonyl group as opposed to the imine group. This provides compounds for a broad-based study of the thermolyses of substituted iminocyclobutenes. These reactions show similarity to those of the analogous cyclobutenones. That is, they are initiated by 4 π -electrocyclic ring opening, followed by 6 π -electrocyclic ring closure to give aminophenols or aminonaphthols. It was demonstrated that the products show reversed regiochemistry as compared with the corresponding carbonyl-derived products. Thus, the imino group in iminocyclobutenones can be viewed as a protective group for the more reactive carbonyl group in alkoxy-substituted cyclobutendiones.

A mechanistically more complex reaction was observed for 4-alkynyl derivatives **41**. Here a diradical intermediate is proposed which undergoes ring closure involving the *N*-aryl group to ultimately give cyclopenta[b]quinolines as the primary products. Although the yields of these products have yet to be optimized, the unusual structures give evidence of the versatility of cyclobutenimine chemistry.

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