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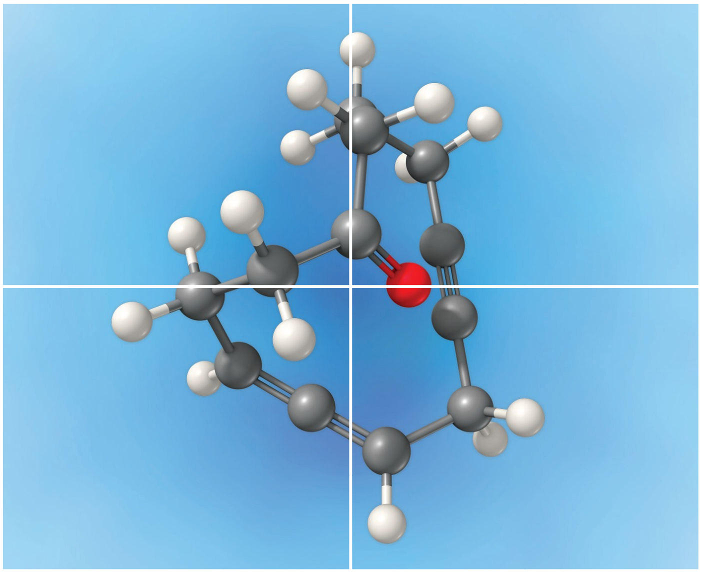

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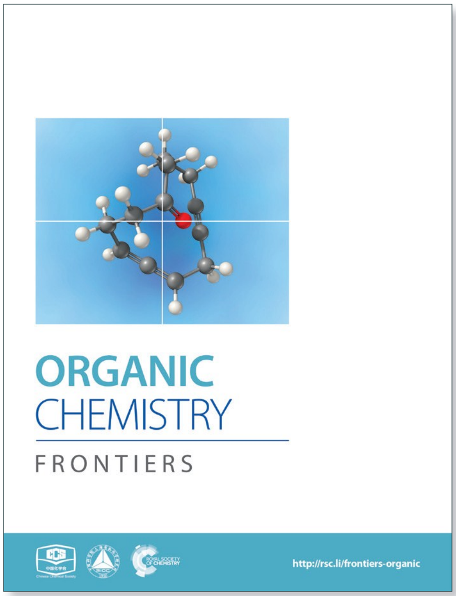

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# The quest for observation and isolation of oxyallyl derivatives.

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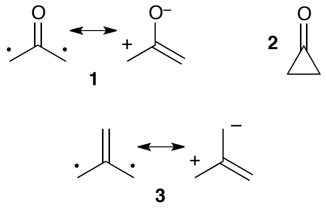
**Abstract:**

This critical review narrates the story of 40 years of attempts to observe and isolate oxyallyl derivatives. These efforts have paved the way to recent achievements, among which the establishment of the transition-state nature of the parent compound and the first observation of an alkyl-substituted oxyallyl. In the recent years, this field of research even reached the critical point, from which oxyallyl derivatives shouldn't be disregarded as chemical oddities anymore, but as attractive synthetic targets with potential applications in advanced materials science.

## 1. Introduction

R. Hoffmann first mentioned 2-(oxy)allyl **1** in 1968. He suggested that the recently synthesized[1] cyclopropanone **2** could in fact adopt a more stable acyclic structure (scheme 1).[2] This hypothesis was essentially supported by extended Hückel calculations and was finally ruled out a year later, when microwave spectroscopy experiments ascertained the cyclic structure of **2**.[3] This short controversy had the virtue of drawing some attention to a new family of compounds, generally denoted as “oxyallyls”. In addition to the synthetic challenge they were offering to chemists, their study was also motivated by the need to investigate their intriguing electronic structure. Indeed oxyallyls belong to the class of non-Kekulé molecules. Their neutral π-system cannot be assigned to a classical Kekulé-type structure, but only to zwitterionic or diradical resonance forms, despite an even number of electrons.[4]



**Scheme 1**. Oxyallyl **1**, cyclopropanone **2** and tri(methylene)methane **3**.

However, it became rapidly obvious that oxyallyls were considerably more elusive than initially suggested by Hoffmann to the point that even the possibility for their observation had been questioned, not to mention their isolation. Indeed, over the years, oxyallyls have been postulated as intermediates in several rearrangement reactions,[5] including the *in vivo* formation of prostaglandins.[6] Importantly, they have been generated, trapped *in situ* by a large variety of dipolarophiles and found many synthetic applications.[7] In spite of many clues of their existence, they had eluded isolation and even spectroscopic observation until very recently. In marked contrast, the related tri(methylene)methane **3** was observed as early as 1966 by EPR at 88 K.[8]

Over more than 40 years, successive publications have highlighted how especially challenging was the study of this class of compounds. Remarkable contributions allowed for a better comprehension of the issues at stakes, and have paved the way to the design of observable versions. In this critical review, we tell the story of the quest for the observation and isolation of oxyallyl derivatives, from the early attempts in the 70-80’s to the recent reports of stable forms.

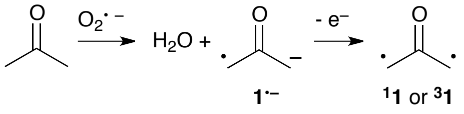
## 2. Parent oxyallyl $H_2C(CO)CH_2$

### *2.1 Can the parent oxyallyl be observed?*

The specific challenge of detecting the parent oxyallyl $H_2C(CO)CH_2$ **1** has been interpreted in term of singlet-triplet gap. Indeed, the disrotatory ring closure of the putative singlet $^1$**1** into cyclopropanone **2** had been predicted to occur with a negligible barrier, if any.[9] Therefore only a triplet ground state is likely to be persistent enough to be easily observed.

We already mentioned the early observation of the related tri(methylene)methane **3**. This compound benefits from of triplet diradical ground state, which is well separated from the lowest singlet state by 16 kcal.mol$^{-1}$.[10] This is a direct consequence of Hund's rule, as the two highest occupied molecular orbitals of **3** are degenerated, non-bonding and non-disjoint.[11] The case of **1** is not so clear-cut. Indeed the lower symmetry of **1** results in a lifting of the degeneracy of the two highest occupied molecular orbitals, which favours the singlet state $^1$**1**. In fact, several calculations predicted a singlet-triplet gap as small as 0.3 kcal.mol$^{-1}$, but still in favour of the triplet $^3$**1**. Importantly, Schwarz *et al.* reported very small computed spin-orbit elements, which are expected to contribute the most to the triplet-singlet transition, and concluded that this may be sufficient to allow for the detection of $^3$**1**. However, the attempts of these authors to identify **1** by neutralization-reionization mass spectroscopy were inconclusive.[12,13]

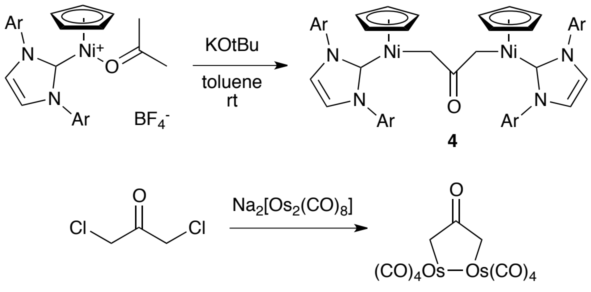
In 2009, Lineberger *et al.* reported a negative ion photoelectron spectroscopy study of the oxyallyl radical anion **1$^{\bullet-}$**, which could be generated by the gas phase reaction of acetone and the oxygen radical anion $O^{\bullet-}$ (scheme 2).[14] The adiabatic formation of both $^1$**1** and $^3$**1** could be unambiguously deduced from the photoelectron spectra. This remarkable set of experiments provided major fundamental answers about the nature of **1**. First, the authors could determine that, contrary to the predictions of earlier theoretical studies, $^1$**1** is slightly more stable than $^3$**1** by 1.3 kcal.mol$^{-1}$. Moreover, significant broadening of the photoelectron spectra indicated that $^1$**1** corresponds in fact to a transition state! Therefore, 40 years after Hoffmann's initial proposal, it could be concluded that **1** is not a genuine intermediate, but an energetic maximum along the stereomutation of the methylenes of cyclopropanone **2**.



**Scheme 2**: Observation of $^1$**1** and $^3$**1** by negative ion photoelectron spectroscopy.

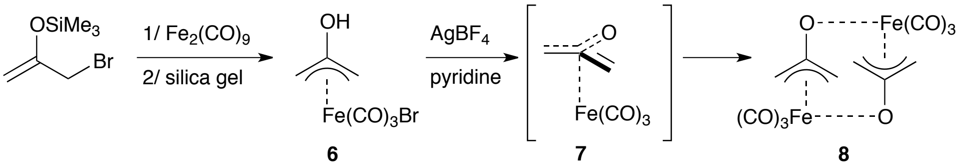
### *2.2 Transition metals complexes of **1**.*

Complexation to transition metals is a classical strategy to isolate otherwise transient species. Several complexes featuring a 2-(oxy)allyl pattern have been reported in the literature. For instance, the dinickel complex **4**, which features a $CH_2(CO)CH_2$ bridge, was synthesized by deprotonation of the corresponding cationic nickel(II)-acetone complex, isolated and fully characterized.[15] Note that although **4** was presented as featuring a trapped oxyallyl ligand **1**, it is certainly better described as two nickel(II) centres bridged by the bis-anion $\mathbf{1}^{2-}$. Similarly, osmium complex **5** is a di(metalla)cyclopentanone (scheme 3).[16]



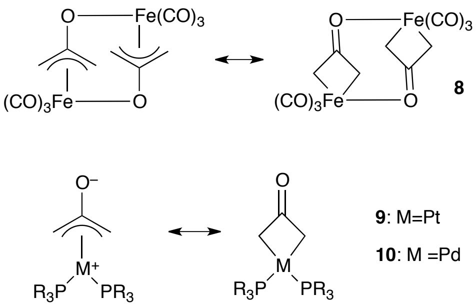
**Scheme 3:** synthesis of di**(**metalla)ketones **4** and **5**.

The 2-(hydroxy)allyl iron complex **6** was synthesized from silylenol ether and isolated. Its deprotonation (pKa = 5.2) in presence of a bromine scavenger didn't afford complex **7**, but its head-to-tail dimer **8** (scheme 4). Interestingly, the tri(methylene)methane equivalent is monomeric.[17]



**Scheme 4**: synthesis of complexes **7** and **8**.

Related monomeric complexes of $\mathbf{1}^{2-}$ with platinum(II) and palladium(II) have been reported (compounds **9** and **10**, scheme 5).[18] Such π-allyl complexes may appear as more satisfying models for "stabilized" coordinated oxyallyls than **4** or **5** because they maintain a formal 4-centers π-system on the ligand. According to spectroscopic and structural studies, both π-allyl and metallacyclobutane mesomeric forms are significant in iron and platinum complexes (**8** and **9**). Palladium complexes **10** have a dominant π-allyl character.



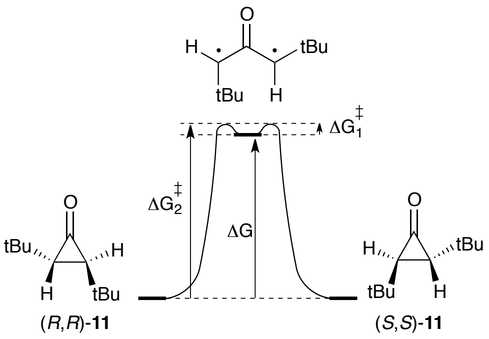
**Scheme 5**: the metallacyclobutanone and π-allyl mesomeric forms of **8-10**.

## 3. Alkyl substituted oxyallyls.

### *3.1 Decreasing the oxyallyl-cyclopropanone energy gap*

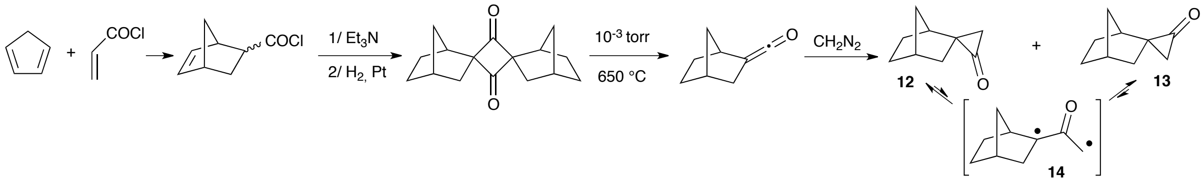
Contrary to their parent compound **1**, alkyl and aryl substituted oxyallyls are predicted to be genuine species, which unambiguously correspond to minima on energy hypersurfaces. However, because of their singlet ground state, their cyclisation into the corresponding cyclopropanone is predicted to occur with very low activation barriers.[9d] Therefore, any reasonable model for an isolable oxyallyl requires a situation in which the cyclopropanone form is made less stable than the oxyallyl.

Estimates of the oxyallyl-cyclopropanone Gibbs energy difference ($\Delta G$) have been deduced from studies of the stereomutation of cyclopropanones. Indeed, as the barrier for cyclisation of the oxyallyl $\Delta G_1^{\neq}$ is very small, $\Delta G$ can be reasonably approximated to the barrier for the ring opening into the corresponding oxyallyl $\Delta G_2^{\neq}$ (scheme 6). In 1970, Greene *et al.* reported the partial resolution of trans-2,3-di(*tert*-butyl)cyclopropanone **11** by asymmetric destruction with *d*-amphetamine. Monitoring of the racemization of enantioenriched samples of **11** afforded $\Delta G$ values of 27-29 kcal.mol$^{-1}$, depending of the solvent.[19]



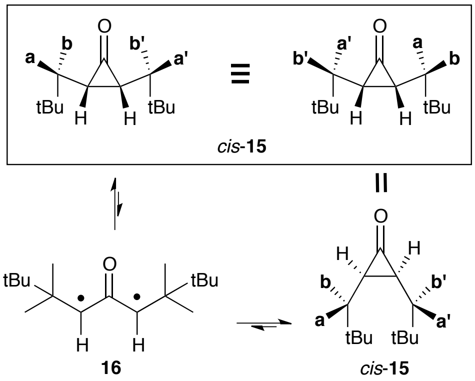
**Scheme 6:** Thermal racemization of trans-2,3-di(*tert*-butyl)cyclopropanone **11**.

Twenty years later, Cordes and Berson reported a multi-step synthesis of two epimers of spiro(bicyclo[2.2.1]heptane-2,1'-cyclopropan)-2'-one from cyclopentadiene and acryloyl chloride (scheme 7).[20] The authors measured $\Delta G$ values of 16-19 kcal.mol$^{-1}$ for the interconversion of spiro-cyclopropanones **12** and **13** (through **14**). Compared to **11**, this corresponds to a decrease of about 45% for the oxyallyl-cyclopropanone energy gap.



**Scheme 7:** Synthesis and dynamic exchange of epimeric cyclopropanones **12** and **13**.

This latter result demonstrated that modulation of steric effect could allow for significant destabilization of cyclopropanones with regard to their oxyallyl form. It prompted Sun and Sorensen to investigate a series of sterically hindered *cis*-cyclopropanones.[21] In the case of *cis*-**15** (with 2-(3,3,2-trimethyl)butyl substituents, see scheme 9), they observed the coalescence of $^1$H NMR signal of the two pairs of diastereotopic methyls, which are well resolved below 200K. They attributed this phenomenon as being the result of the disrotatory opening of cis-**15.** Indeed, the resulting oxyallyl **16** can undergo disrotatory ring closure in two opposite directions, resulting in a formal scrambling of the pairs of methyls (scheme 8).

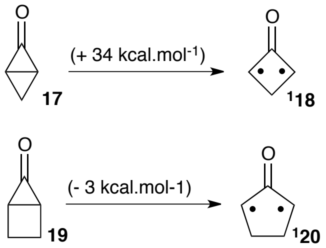


**Scheme 8**: Exchange of diastereotopic methyls of *cis*-**15** upon formation of oxyallyl **16**.

From the dynamic NMR study in chloroform, the authors deduced a Gibbs energy gap of 9.8 kcal.mol$^{-1}$ between *cis*-**15** and **16**. According to this remarkably low value, a 1M solution of *cis*-**15** should contains about 60nM of **16** at 25°C. In principle, oxyallyl **16** reaches detectable levels at such concentration. However, the experimental observation of this compound would require ultra-pure solution of *cis*-**15** to allow for an unambiguous identification.

### *3.2 Destabilization of cyclopropanones with fused polycyclic structures.*

In 1990, Lahti *et al.* reported a computational study of fused bicyclic cyclopropanones.[22] Bicyclo[1.1.0]butanone **17** was found significantly more stable than its corresponding oxyallyl **18** by 34 kcal.mol$^{-1}$. On the other hand, bicyclo[2.1.0]pentan-5-one **19** lied +3 kcal.mol$^{-1}$ above the oxyallyl form **20** (scheme 9). This can be interpreted as the result of the difference in ring-strain situation in the two systems. Indeed, the case of **20** is optimal: it features a five-membered ring with no major ring strain, whereas fused 3-membered and 4-membered rings thermodynamically disfavour the corresponding cyclopropanone **19**. On the contrary **18** remains involved in a strained 4-membered ring. Of note, both oxyallyls were predicted to have a singlet diradicaloid ground state and a modest singlet–triplet gap of 4–6 kcal.mol$^{-1}$.

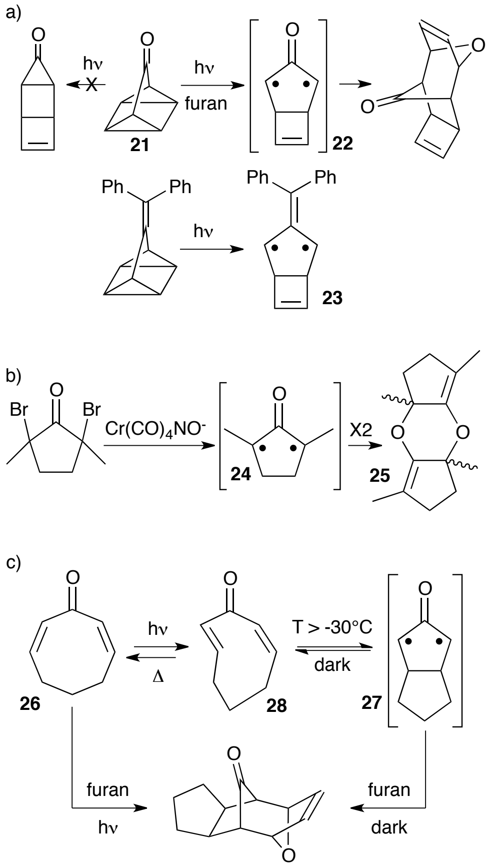


**Scheme 9:** Stability of fused cyclopropanones in respect with their oxyallyl forms.

There are several reports of attempts to observe oxyallyls that are related to **20**. Ikegami *et al.* showed that photolysis of polycyclic compound **21** generated oxyallyl **22**, which could be trapped by various dipolarophiles, including furan (scheme 10a). However, all attempts to observe **22** failed. In marked contrast, the related tri(methylene)methane derivative **23** could be generated in the exact same conditions and observed by EPR in methylcyclohexane matrix at 77 K.[23]

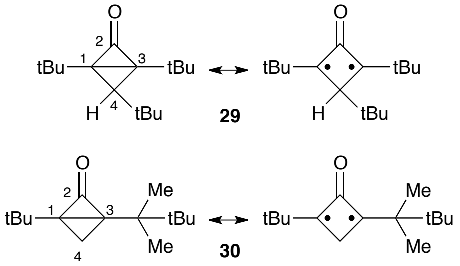
Sorensen et al. demonstrated the formation of oxyallyl **24** by several trapping experiments upon *in situ* reduction of the corresponding dibromoketone (scheme 10b).[24] Needless to say, **24** lacks the destabilizing fused cyclobutene ring of **22**, and therefore is a far better candidate for a persistent oxyallyl. Unfortunately, in the absence of trapping agent the authors couldn't observe **24**, but the "instantaneous" formation of its head-to-tail dimer **25**. They could only conclude that the $t_{1/2}$ for the dimerization of **24** must be lower than 10 minutes at -120°C.

As early as 1968, Crandall et *al.* noticed that irradiation of 2,7-cyclooctadienone **26** at -78°C followed by addition of furan in absence of light afforded the same cycloadduct that was obtained upon irradiation of **26** in presence of furan (scheme 10c).[25,26] This indicated the formation of a persistent reactive intermediate. Of course, in light of the above-mentioned computational studies, it is tempting to hypothesize the formation of oxyallyl **27**. In 1999, Raulerson *et al.* reinvestigated this reaction and showed that the intermediate was in fact the strained *trans,cis*-cyclooctadienone **28**, which can undergo thermal cyclisation above -30°C to afford the oxyallyl **27**.[27] Note that **26-28** are in equilibrium under irradiation and about 20% of **26** is converted into **28** at the photostationary state. Therefore it is likely that **27** is unobservable because its fast thermal ring-opening in absence of light recreates the most stable cyclooctadienone **26**.



**Scheme 10:** reported attempts to observe oxyallyls related to **20**.

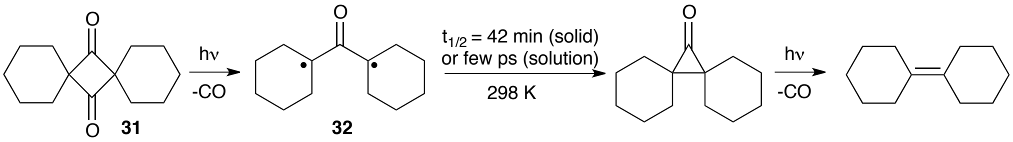
Bicyclo[1.1.0]butanones had been disregarded for long as potential entries to oxyallyls, because the ring-opening of **17** was predicted to be strongly thermodynamically disfavoured. Another obstacle to the study of these bicyclic compounds, and not the least, is their high reactivity and the ensuing difficulty of their synthesis. The first X-ray structure of isolable representatives, the *tert*-butyl substituted bicyclo[1.1.0]butanone **29** and **30**, was reported in 2005 by Sorensen *et al.*.[28,29] Ironically, spectroscopic and structural data clearly show that bicyclo[1.1.0]butanones have a hybrid structure with a non-negligible oxyallyl character (scheme 11). For instance, the NMR chemical shifts of the fused carbons C1 and C3 are significantly deshielded (67-81 ppm) compared to monocyclic cyclopropanones (29-36 ppm). Furthermore, compounds **29** and **30** feature especially long C1-C3 bonds (about 170 pm, compared to 157 pm in **1**)[3] and a distinctly pyramidal ketone functionality ("out of plane" angle: 12–21°). Unsurprisingly, the thermal evolution of bicyclo[1.1.0]butanones is reminiscent of oxyallyls.



**Scheme 11**: The oxyallyl–bicyclo[1.1.0]butanone hybrid structures of **29** and **30**.

### *3.3 Observation of alkyl-substituted oxyallyls in the solid state.*

In 1991 Garcia-Garibay *et al.* reported a new strategy to tackle the issue of the ultra-fast formation of cyclopropanones. They envisioned that oxyallyls generated in the solid state should undergo slower ring-closures, and therefore may be easier to detect. They studied the photo-induced decarbonylation of crystalline samples of spiro-dione **31** and observed a deep blue product, which could be identified as the di(cyclohexyl)oxyallyl **32**. The decay of this compound in the solid state was remarkably slow, with a half-life of 42 minutes at 298 K!  Note that the ensuing cyclopropanone was observed, but couldn't be isolated due to its decomposition under irradiation to afford dicyclohexylidene by loss of CO (scheme 12).[30]

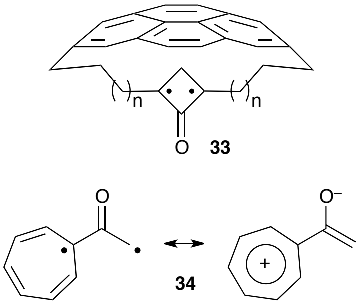


**Scheme 12**: generation and evolution of oxyallyl **32**.

Interestingly, the authors also measured the transient absorption spectra of **31** in solution upon excitation by 150 fs laser pulses. Once again they could observe the formation of the oxyallyl and measured half-lives of 1–8 ps, depending of the solvent. These results mark a pivotal milestone in the study of alkyl-substituted oxyallyl intermediates. They also illustrate the specific challenges of detecting these species. Indeed, in contrast with tri(methylene)methanes, EPR cannot allow for easy and unambiguous observations. As a matter of fact, without the guidance of the univocal spectroscopic observation of **32** in the solid state, it is likely that the interpretation of transient absorption spectra in solution would have been inconclusive.

### *3.4 Perspective and potential synthetic targets*

The quest for the observation of alkyl-substituted oxyallyls hasn't reached its conclusion yet. The above-mentioned results clearly paved the way for the design of persistent versions. For example, it is likely that derivatives of **24** can be sheltered from dimerization by more sterically demanding substituents. Interestingly, theoretical studies have suggested several potential alternative synthetic targets, such as compounds **33**, in which the stretch effect of a macrocyclic ring is predicted to push the hybrid structure of bicyclo[1.1.0]butanones towards a genuine oxyallyl form (scheme 13).[31] Another possible strategy is to stabilize a zwiterionic form by introducing groups that stabilize positive charges. Hess reported a computational study of derivatives with cyclopropenyl, cyclopentadienyl and cycloheptatrienyl moieties. He found oxyallyl **34** more stable than its cyclopropanone and allene oxide forms, by 5.4 and 10.7 kcal.mol$^{-1}$ respectively, and suggested that it could be observable in an appropriate environment.[32]

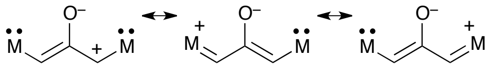


**Scheme 13:** possible synthetic targets suggested by computational studies

## 4. Stable hetero-substituted derivatives

### *4.1 Donor-stabilized oxyallyls*

Extension of delocalized π-systems is a traditional method to achieve significant stability. In the case of oxyllallyls, the introduction of +M donating groups seems the most appropriate, since it strongly stabilizes the cationic allylic moieties in the zwitterionic resonance form (scheme 14). In addition, push-push patterns are likely to preclude the formation of the cyclopropanone forms.

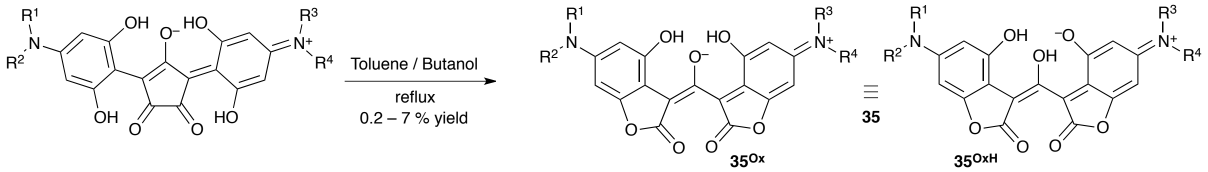


**Scheme 14**: Stabilization of oxyallyls by +M donating substituents.

Scarce examples of such species can be found in the literature. In 2003, Tian *et al.* reported the synthesis of a series of compounds **35** from the thermal rearrangement of some croconaines featuring 4-amino-2,6-(dihydroxy)phenyl substituents (scheme 15).[33] These compounds are near IR-dyes that are attractive for the design of non-linear optic materials, due to their propensity to form J-aggregates on spin-coated films.[34]

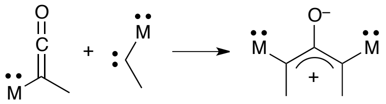
Molecules **35** could be seen as examples of oxyallyl centres with two +M donating 4-aminophenyl groups. However, the sharing of two protons by three hydroxy groups blurs the genuine structure of **35**. Interestingly, examination of X-ray diffraction data reveals that the C-O bonds in the phenoxy and the formal oxyallyl moieties have similar lengths (132-133 pm). Therefore, although they have been depicted as a H-bond stabilized oxyallyl (structure $\mathbf{35^{Ox}}$), they can be described just as well as protonated oxyallyl cations interacting with phenoxy groups (structure $\mathbf{35^{OxH}}$).[35]

The rearrangement of croconaines is of limited practical interest because of low yields and the narrow range of accessible structures. However, the stability of **35** suggests that the introduction of stabilizing H-bonds must be a good strategy for the design of new stable hetero-substituted oxyallyl derivatives.



**Scheme 15**: synthesis of **35** from low-yield rearrangement of croconaines.

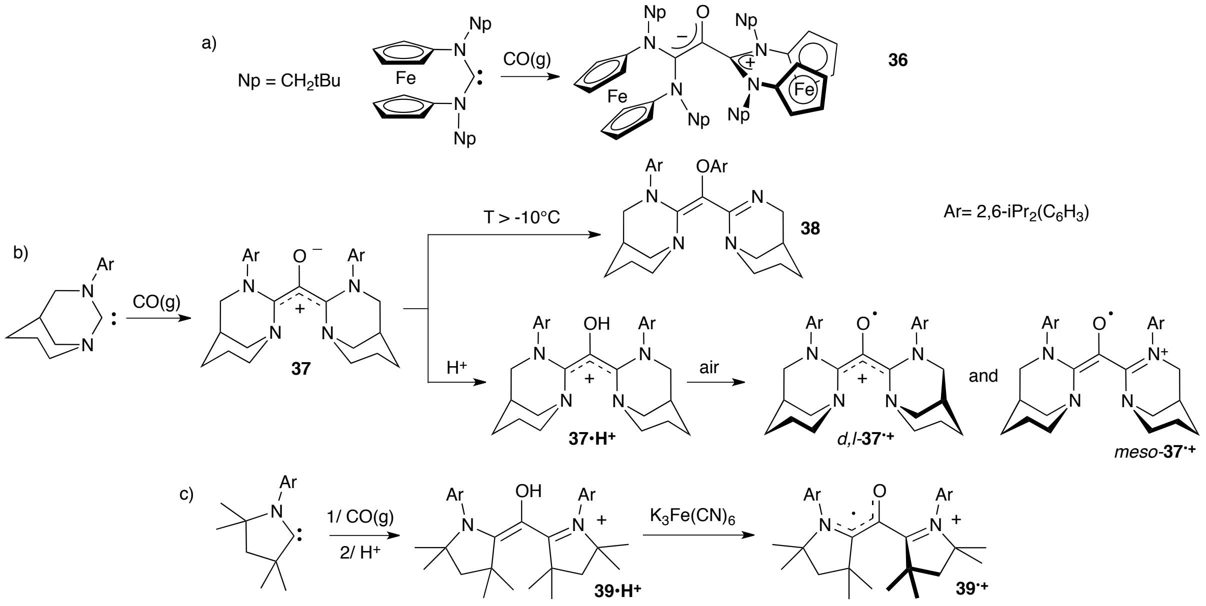
Another synthetic strategy could rely on the reaction of carbenes with ketenes, which is a known method for generating transient oxyallyls.[36] In principle, this reaction could be extended to the formation of stabilized 1,3-di(hetero-substituted)oxyallyls, especially 1,3-di(amino)oxyallyls (scheme 16). However, aminoketenes are only available from the addition of stable (amino)carbenes on carbon monoxide.[37-41] The scope of this reaction is limited to few stable electrophilic carbenes and doesn't include the classical cyclic di(amino)carbenes, which don't react with CO.[42] Furthermore, the steric bulk of stable carbenes usually preclude the addition of a second equivalent, which would afford the corresponding oxyallyl.



**Scheme 16**: hetero-substituted oxyallyl from the addition of carbenes to ketenes.

Siemeling at al. first reported the addition of carbon monoxide to two equivalents of a ferrocene-based carbene in 2010.[38a] However, the resulting product **36** features two orthogonal carbene units, only one being conjugated with the carbonyl. Therefore **36** has the structure of a zwitterrionic enolate, not an oxyallyl (scheme 17a).

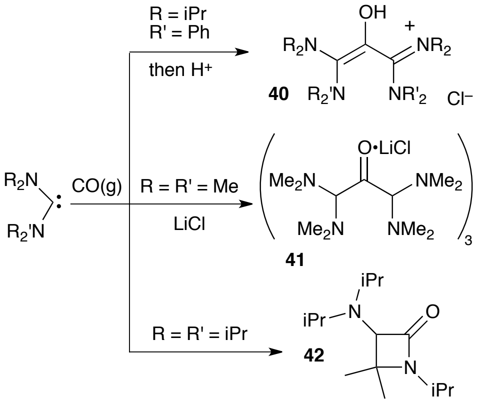
In 2013 we showed that bubbling CO in a solution of an anti-Bredt diaminocarbene at -78°C affords the deep-blue amino-substituted oxyallyl **37**.[39] Compound **37** was characterized by NMR, but couldn't be isolated, as it rearranges into **38** above -10°C. Protonation of **37** yields the oxyallyl cation **37•H**$^+$, which was fully characterized, including a single crystal diffraction study (scheme 17b). Similarly oxyallyl cation **39•H**$^+$ could be obtained from a cyclic (alkyl)(amino)carbene featuring small substituents (scheme 17c).[40]



**Scheme 17**: Reaction of stable unhindered electrophilic cyclic carbenes with carbon monoxide.

Oxyallyl cations **37•H**$^+$ and **39•H**$^+$ were oxidized into their corresponding radical cations **37**$^{\bullet+}$ and **39**$^{\bullet+}$, respectively.[39,40,43] Surprisingly, these compounds are very stable toward air and moisture. Radical **39**$^{\bullet+}$ has been stored for years as a solid and has a half-life of about a week in aerated technical solutions. Even more remarkably, both diastereomers of **37**$^{\bullet+}$ could be crystalized under aerobic conditions from refluxing technical toluene solutions. Note that only one carbene unit of *meso*-**37**$^{\bullet+}$ and **39**$^{\bullet+}$ is involved in the radical stabilization, the π-system of the second unit being orthogonal to the SOMO. Thus, they are better depicted as (amino)(carboxy)radicals with a cationic spectator substituent. In contrast, *d,l*-**37**$^{\bullet+}$ is a genuine one-electron oxidized oxyallyl, with a fully delocalized π-system on the carbonyl and both carbene moieties.

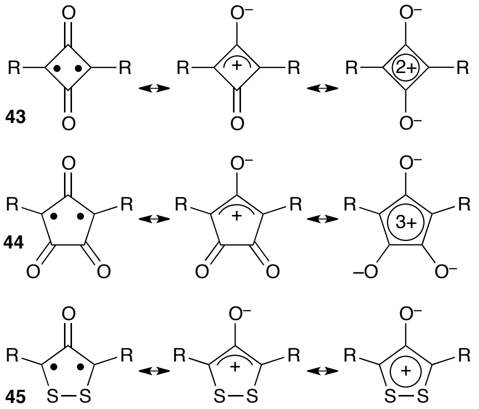
Siemeling *et al.* also reported reactions between acyclic di(amino)carbenes and CO.[41] They were able to isolate oxyallyl cation **40** and the trimeric oxyallyl–lithium chloride complex **41**. To date, the X-ray structure of the latter is certainly the closest available picture of a genuine amino-substituted oxyallyl. Note that, here again, the scope of the reaction is limited to few small amino groups. Indeed, the authors showed that the formation of β-lactams, such as **42**, is favoured by more bulky substituents (scheme 18).



**Scheme 18**: Reaction of stable acyclic di(amino)carbenes with carbon monoxide.

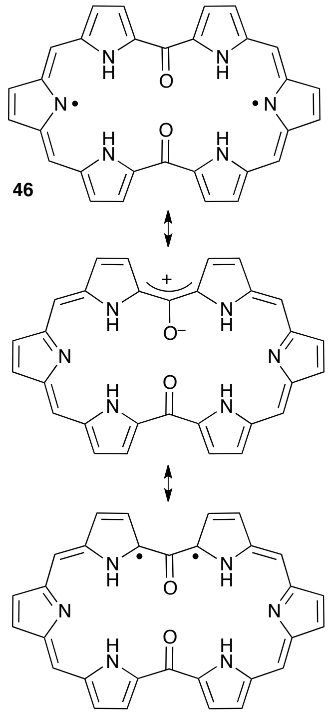
### 4.2 Non-Kekulé aromatic compounds with a formal oxyallyl pattern

Several cyclic conjugated non-Kekulé compounds contain a formal oxyallyl pattern. As shown on scheme 19, squaraines **43**, croconaines **44** or dithiolane derivatives **45** can be depicted as zwitterionic aromatic rings, but also feature oxyallyl-type diradical and zwitterionic resonance forms. Compounds **43** and **44** exhibit intense π–π* transitions and have attracted considerable attention as promising near-IR dyes.[44] For long, their oxyallyl character had been disregarded, their absorption being attributed to a classical donor-acceptor charge transfer between the central ring and electron-donating substituents. However, in the last decade, several theoretical studies demonstrated that the excitation was predominantly localized at the central ring, the low-energy transitions reflecting a significant diradicaloid character of the molecules.[45]



**Scheme 19**: Non-Kekulé dyes with an oxyallyl pattern (R is an electron-donating group)

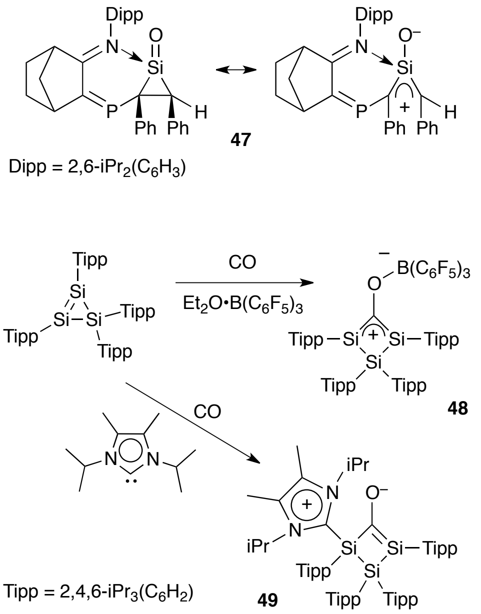
An oxyallyl pattern can also be identified in the structure of diketohexaphyrin **46** (scheme 20). This compound has a strong 26 π–electron aromatic character and is remarkably stable towards air and moisture. It is a non-Kekulé molecule with a singlet diradical ground state. The triplet state is very close in energy (+2.5 kcal.mol$^{-1}$), as shown by EPR and magnetic susceptibility measurements.[46]



**Scheme 20**: resonance forms of non-Kekulé compound **46**.

### *4.3 Silicon-based oxyallyls*

The recent progresses in the quest for isolable oxyallyls also inspired few synthetic studies in the silicon series. Importantly, although carbon and silicon are both group 14 elements, they strongly differ in terms of electronegativity, atomic radii, capacity for hypervalence, etc. Therefore silaoxyallyls offer a distinct problematic from their carbon analogues. Whereas carbonyls are common organic functionalities, silacarbonyl compounds remain elusive, being only isolated as adducts with Lewis bases. Kato et al. reported the first silanone (a “sila”ketone) Lewis-base adduct **47** in 2013 only. [47] Interestingly the authors demonstrated that **47**, which is a donor-stabilized silacyclopropanone, has a hybrid structure with a significant silaoxyallyl character (Scheme 21).



**Scheme 21**: Stabilized silacyclopropanone **47** and silaoxyallyl derivatives **48–49**.

A year later, Scheschkewitz et al. reported the isolation of the Lewis acid adduct of sila-oxyallyl **48** from the reaction of carbon monoxide with a cyclotrisilene, in presence of $B(C_6F_5)_3$. Conversely, when performing the reaction in presence of a stable N-heterocyclic carbene, the donor-stabilized sila-oxyallyl **49** was isolated.[48] Here again, the situation contrasts with carbon-based compound, the carbon analogues of **48** and **49** being unknown and unlikely to be isolated.

## 5. Conclusion

For long, the quest for the observation of oxyallyls derivatives had faced seemingly intractable issues. An abundant literature bears witness of unsuccessful attempts by several research groups. We would like to stress the importance of these publications, which have clearly paved the way to the recent achievements. This is certainly a teachable lesson and one has to wonder whether such apparent "failures" would be published and made available to the community today.

Pivotal advances have marked the last decade, among which the establishment of the transition-state nature of the parent compound **1** and the observation of alkyl-substituted oxyallyl **32**. Theoretical calculations have played a key role in ascertaining the identification of the new compounds. They also unveiled the unexpected oxyallyl character of bicyclo[1.1.0]butanones and compounds **43-45**, which had been mistakenly considered for long as classical cyclopropanones or donor-acceptor-type dyes respectively.

The scene is set for new synthetic challenges. We already showed that the design of highly persistent alkyl-substituted oxyallyls is within reach, and we even discussed a few possible strategies to achieve this goal. Another type of stable oxyallyl derivatives relies on the introduction of strong +M donating 1,3-substituents, favouring singlet zwitterionic limit forms. The small singlet-triplet gap of these species allows for considering potential applications in the field of functional near-IR dyes. Furthermore, preliminary results also revealed original redox properties. For example, the radical-cation of oxyallyls **37** and **39** proved to be remarkably air-stable. However, very few models of oxyallyl featuring such “push-push” substitution are available. Their synthesis relies on reactions with narrow scopes: the low yield rearrangement of some croconaines and the carbonylation of rare non-bulky electrophilic stable carbenes. It is clear that further development in this field will require more general and versatile synthetic routes to be designed in the future.

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