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CARBENES AND CARBENOIDS WITH NEIGHBORING HETEROATOMS

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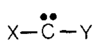
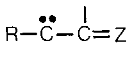
CONTENTS

1. INTRODUCTION

Substituent effects on carbene and carbenoid reactivity have sustained a high level of attention over the past 15 years. Of primary interest has been the effect of substituents directly bound to, or conjugated with, the carbene or carbenoid center. Thus, recent work and reviews[1] have appeared covering, for example, the chemistry of species related to **1**,[1a,b] **2**,[1c-h] and unsaturated carbenes, **3**.[1e,i] These will not be reviewed here. This report will review the chemistry of carbenes and carbenoids bearing heteroatom substituents which affect the chemistry of, but are insulated from direct conjugation with the carbenic C atom. Thus, the reactions of remote C=C double bonds, including the vinylcyclopropylidene to cyclopentenylidene rearrangement,[1h] these having been recently reviewed elsewhere,[1d-f,h] are not reviewed herein. The term "carbenoid" is used here in the same (structural) sense it has been used by Köbrich,[2] i.e. to denote compounds, often α-haloorganolithium compounds, that have a metal atom and a leaving group on the same C atom. Thus, the chemistry of transition metal–carbene "complexes" is not reviewed herein. Where possible, we will contrast the behavior of the heteroatom-containing compounds with that of appropriate C atom-containing analogs, and reiterate, or attempt to provide, a mechanistic rationale for the chemistry.


$X-\overset{\bullet\bullet}{C}-Y$

1


$R-\overset{\bullet\bullet}{C}-\overset{|}{C}=Z$

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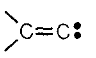

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As can be seen from the table of contents the list of neighboring groups is heavily weighted with n electron donating groups. While neighboring group participation by such groups in carbenium ion chemistry has been extensively and systematically studied, no study of such magnitude has been made for its companion 6-electron species, the carbene. Gleiter and Hoffmann[3] have used Extended Hückel calculations to investigate the stabilization of singlet (vs triplet) nitrene and carbene by remote electron donating groups. They concluded that the singlet state of carbene (or nitrene) could be stabilized by the symmetrical approach of two nonbonding electron pairs along the axis of the empty p orbital. However this three center bonding arrangement, while further stabilized by the presence of d orbitals in the system, was predicted to be less stable than a two center bond formed by approach of a single nonbonding electron pair.[3a] Also, a suitably positioned, remote π electron pair was predicted to stabilize a singlet carbene center *via* the "foiled methylene addition reaction",[3b,4] e.g. **4**→**5**. From the foregoing

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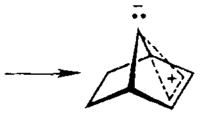

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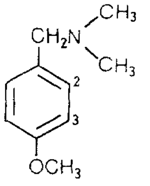

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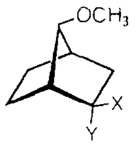


7 a X = Br, Y = H
b X = H, Y = Br

one would predict that remote n electron donating substituents would alter the chemistry of carbenes. Such a prediction would have found experimental support in the prior work of Kirmse[5] and Schecter[6] (to be discussed in turn) on the migration of ether and thioether groups to carbenic centers.

Carbenes are most commonly produced by photolysis or thermolysis of diazoalkane derivatives and by thermolysis of α-haloorganometallic compounds (carbenoids). These latter entities are most often produced by halogen–metal exchange (e.g. 1) or by direct metallation (2). The presence of an electron donating substituent in the starting materials for reactions (1) and (2) could well be expected to affect both the formation and stability of the resulting carbenoid. For example the amino group of **6** directs

(1)

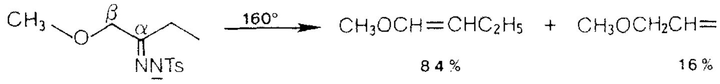
(2)

lithiation by BuLi to the less acidic 2-position;[7] and o-lithioanisole has been shown to be more thermodynamically stable than the para isomer.[8] Also, the *syn*-7-OMe group of **7a** dramatically enhances the rate of Br–Li exchange (with n-BuLi) compared with **7b** and the *anti*-7-OMe isomer of **7a**, a result interpretable in kinetic or thermodynamic terms.[9] Thus, in these cases, an intramolecular metal ion solvating group could alter the electrophilic and nucleophilic properties of a carbenoid. In what follows the nucleophilic properties of carbenoids will be touched on, but the emphasis will be on the electrophilic reactions of the carbenes and carbenoids.

2. SYSTEMS WITH NEIGHBORING OXYGEN FUNCTIONS

(A) *Ether groups*

Bamford–Stevens reactions. The effect of β alkoxyl substituents on H-migration to a carbenic center has been summarized previously.[1d,10] In short, a β-alkoxyl substituent substantially enhances the



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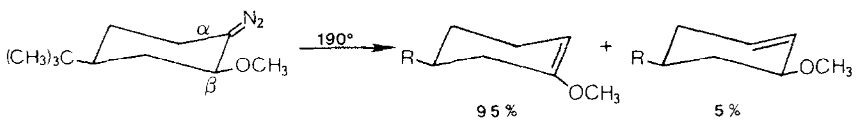
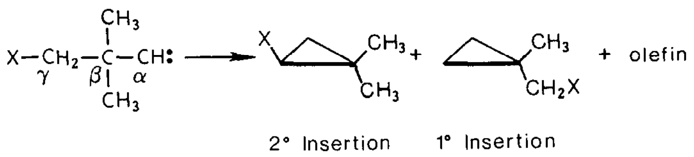


9

migration of H to the carbene center as illustrated by the cases of **8**[5,10] and **9**.[12] Similar results are obtained when the carbenes are generated photochemically. The results point to the development of positive charge at C β, stabilizeable by resonance electron donation of the OMe group.

Intramolecular C-H *insertion.* Ether substituents may either enhance or retard the insertion of a singlet carbene into a sterically available, proximate C–H bond and the result obtained depends on the location of the O substituent in the molecule. Kirmse[10,11,13] has examined the effect of γ-heteroatom substituents on the cyclopropane-forming (γ) C–H insertion reaction of compounds **10**. Heteroatom substituents X reduce the proportion of insertion into a secondary, proximate C–H bond, and with OMe the effect is rather dramatic. While the transition state for secondary C–H insertion is more crowded than that for primary C–H insertion the effect is not a steric one. With alkyl groups of bulk comparable to (or larger than) the X substituents, a higher 2°/1° insertion ratio is obtained.

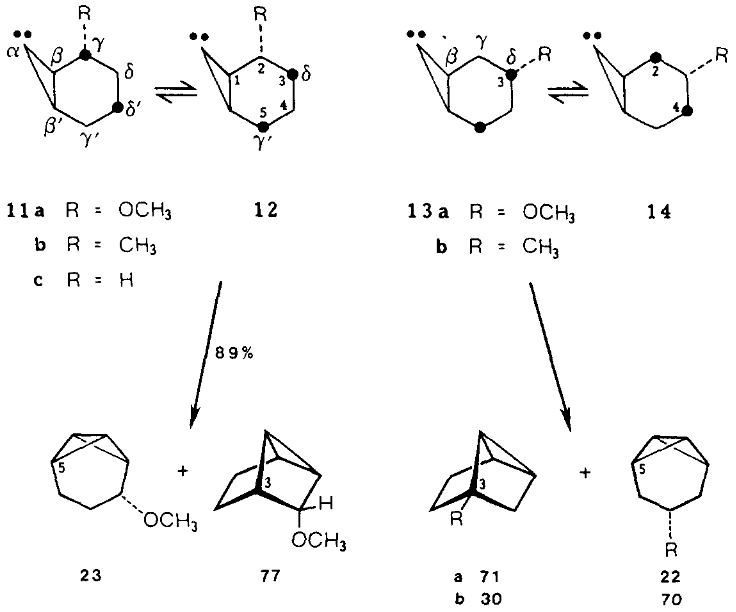


10

X	CH_3—	C_2H_5—	i-C_3H_7	n-C_3H_7—
2°/1°	0.78	0.85	0.95	0.95

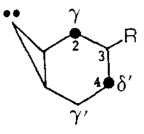
X	CH_2=CH—	C_6H_5—	$(CH_3)_2N$—	CH_3O—
2°/1°	3	0.5	0.21	0.06

Paquette[14] has examined the intramolecular C–H insertion reactions of a series of 7-norcaranylidenes, prepared by reaction of the corresponding 7,7-dibromo compounds with ethereal MeLi at −10°. Some key results on the effect of γ and δ positioned OMe groups are summarized with the aid of Scheme 1. Carbene (or carbenoid[15]) **11a**, reacting exclusively in conformation **12a**, gave, in good yield,

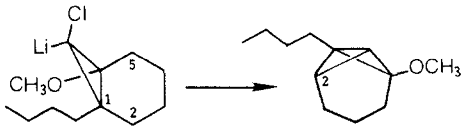


Scheme 1.

products of insertion into the *syn*-axial C–H bonds at positions 3 (77%) and 5 (23%). These results can be contrasted with those obtained with **11b** which (reacting in that conformation) gave insertion into C2-H exclusively. Further, the reactivity patterns of **11c** norcaranylidene itself, and the conformationally fixed homolog **15a** indicate γ/δ' C–H insertion ratios of 24 and 25 respectively.[17] While, there's no *a priori* reason for **12a** to be the more stable (and more populous) conformation, it is, none-the-less, the more reactive one. Thus, the γ-OMe group of **11a⇄12a** deactivates its proximate C–H bond toward C–H insertion, a result consistent with Kirmse's finding. What's more, the γ-OMe group, *pseudo*-axial in **12a**, *activates* the adjacent δ C–H bond toward C–H insertion giving, in sharp contrast to **11c** and **15a**, a γ'/δ C–H insertion ratio of 0.30. Additional examples of this type of activation are reported in Ref. 14 where Paquette attributes the effect to a "backside" anchimeric assistance, to H transfer, which stabilizes positive charge developing at the δ-C in the transition state.[17b] Carbenoid **16**[18] represents a case where C–H insertion at either C-2 or C-5 is not conformationally precluded. OMe participation in the "backside" sense noted above is precluded, however. The major product of thermolysis (at −70° or −35°) of **16** was **17** (*ca.* 60%), a result due either to inductive deactivation of C5-H by the OMe, or to conformational preference for C2-H induced by the 1-n-Bu group,[19] or to both effects. Paquette[14] attempted to generate the noncaranylidene **15b**. Metal–halogen exchange seemed to proceed normally with the corresponding 7,7-dibromo compound. However the carbenoid, probably possessing an *endo* Li atom solvated intramolecularly by the *syn*-OMe group, and thereby stabilized, failed to yield volatile products of C_7H_9(Me) formulation.



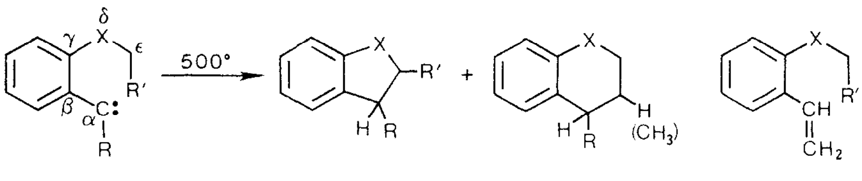
15 a R = t-C_4H_9
b R = OCH_3



16 17

The δ-OMe group of **13a⇄14a** was seen to activate its proximate C–H bond toward insertion by the carbenic center.[14] Thus, **13a**, with the OMe group preferentially equatorial (as expected) underwent C–H insertion at C3 (71%) and at C5 (22%). Reaction in conformation **14a** yielded C–H insertion at C2 (7%). These results stand, again, in contrast to the propensity for noncaranylidenes to insert in γ or γ' C–H bonds as opposed to δ or δ' bonds (see **13b** and the previously noted examples). Kirmse[10,13] interpreted the deactivation of γ C–H insertion by a γ-OMe substituent as due to an inductive effect (ground state effect) which reduced the nucleophilicity of the C–H bond. Much along the same line Paquette[14] has rationalized the results in the noncaranylidine series as indicating an "early" transition state for the γ C–H insertion reaction, one without extensive C–H bond stretching. For δ C–H insertion a transition state later on the reaction coordinate is envisioned, one in which resonance electron donation by O can operate to stabilize positive charge developing at the C atom.

The results of Crow and McNab,[20] who examined a series of aryl carbenes including **18–20**, indicate an activating effect on ε C–H insertion by a proximate O substituent. The carbenes were generated by pyrolysis of tosylhydrazone salts of *ortho* substituted benzaldehydes (**18** and **19**) and acetophenones (**20**) and an excerpt of results is presented in Scheme 2. Competition between 5- and 6-membered ring formation was studied using carbenes **18** and **19**. Examination of the yield ratios of products **21** and **22**



18 R = H, R' = CH_3
19 R = H, R' = C_2H_5
20 R = CH_3 R' = H

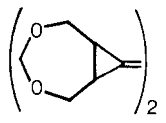
21 22 23

	X:	CH_2	O	NC_2H_5	S
18 →	21/22:	3.0	38.0	24.5	5.3
19 →	21/22:	1.9	14.4	—	2.3
20 →	21/23:	0.8	1.3	15 (NCH_3)	2.0

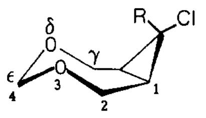
Scheme 2.

reveals a substantial enhancement in the proportion of ε C–H insertion when CH_2 is replaced by O. The authors, using Dreiding stereomodels to evaluate stereochemical effects in the transition state, found that O and N substituents caused no steric perturbation, relative to $X = CH_2$, of the transition state for 6-membered ring formation. For the transition state leading to 5-membered ring formation steric changes due to O and N were present, but small. The authors concluded that the enhancement of 5-membered ring formation by O or N resulted from the substituent's ability to support positive charge, with the differences (anomalies?) in enhancement resulting from the relative demand for such support, in the transition state. Also, for the reasons cited above, O, N and S substituents enable 5-membered ring formation to compete more favorably with the Bamford–Stevens reaction of carbene **20**. (Nitrogen dramatically reduces the yield of Bamford–Stevens product; this is ascribed to a steric effect.)

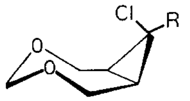
The placement of O substituents on bicyclo[n.1.0]carbon systems has allowed the preparation of stereochemically known, stabilized α-halocyclopropyllithium carbenoids.[18,21,22] This, in turn, has permitted the preparation of epimeric carbenoids[23] and the monitoring of this stereochemical difference on their electrophilic properties. The electrophilic nature of α-haloorganolithium species is well documented. Evidence for their direct involvement in a C–H insertion reaction was obtained by Goldstein and Dolbier[24] who observed a halogen-dependent, primary deuterium isotope effect on γ C–H insertion. (Most recently, ^{13}C spectroscopy has provided direct evidence of electron deficiency at "bromolithio" carbenoid centers.[25] For example, C-7 of *exo*-7-bromo-bicyclo[4.1.0]hept-7-yllithium resonates at $\delta_{TMS}87$, more than 62 ppm downfield relative to the corresponding H-derivative.[25a] Data from other examples point to possible non-sp^3 hybridization.[25b]) Results with epimeric carbenoids, again, implicated a carbenoid in a C–H insertion reaction and demonstrated stereochemical dependence on electrophilic reactivity.[23] Epimeric carbenoids **24b** and **25b** were prepared by Br–Li exchange in ether (−80°) between MeLi (no LiBr) and the epimeric bromochloro-cyclo propanes **24a** and **24b**.[26] Upon thermolysis (near room temp) **24b** gave, almost exclusively, insertion into C4–H. In contrast, **25b** gave products of intermolecular reaction: insertion into solvent (ether), and dimerization to **26**. Conformational analysis using ^1H NMR spectroscopy pointed to a "chaise-lounge" conformation for **24b** (as shown) and a crown conformation for **25b**, but, no conformational factor was evidenced that would preclude **24b** from intermolecular reaction or **25b** from intramolecular reaction. Thus, the epimeric carbenoids reacted with high stereoselectivity. When LiBr was present, thermolysis of **25b**, but not **24b**, became non-stereoselective giving a significant amount of displacement of chloride by bromide (with inversion of configuration). The results point to **24b** as the species undergoing C–H insertion, while a carbene may intervene (partially) in the thermolysis of **25b**. Further, as a pair, **24b** and **25b** display all the reaction types of **11c**: intramolecular insertion, intermolecular insertion and "dimerizing α-elimination". It's tempting to ascribe the observed chemistry of **11c** to its (epimeric) carbenoid precursors. Regarding the all-carbon analog of **24b–25b**, derived from 8,8-dibromo-bicyclo[5.1.0]octane and excess MeLi,[27] it yielded cycloocta-1,2-diene-derived products in 40% yield. Of the remaining carbenoid-derived products, ε C–H insertion (17%), solvent insertion (10%), and reaction with the excess MeLi (33%) accounted for the rest. The two O atoms of **24a–25a** obviously suppress the alkene-forming reaction of cyclopropylidenes, but the lack of γ C–H insertion in the all-carbon system is surprising.



26 syn, anti

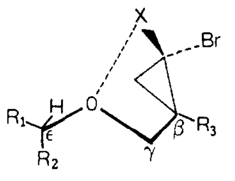


24 a R = Br
b R = Li

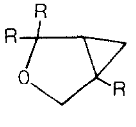


25 a R = Br
b R = Li

Baird[28] has reported a substantial O substituent effect on monocyclic cyclopropylidene electrophilic reactivity. He observed that treatment of dibromocyclopropanes **27a** with MeLi gave, at −30°, the products of ε C–H insertion, (**28**), to almost complete exclusion of the expected allene derivatives. Indeed, treatment of mono- and di-alkyl gem-dibromocyclopropanes with MeLi is an excellent laboratory synthesis of mono- and di-alkyl allenes free of acetylenic isomers,[29] and C–H insertion into the alkyl side chains is not observed. In view of the results with **24b** and **25b** noted above, and the high yield of



27 a R = Br
b R = Li



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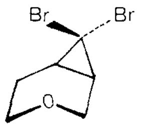
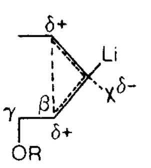


29

endo-Br–Li exchange in the case of 29[21] also, it seems likely that the stabilized carbenoid **27b** is formed and may well be responsible for the observed reactivity change. Coordination of O with Li in **27b** could hold the (activated) C–H bonds of the ε-C atom in closer proximity to the electrophilic center. Also, in the preceding cases of **24** and **25** an O substituent on the γ-C was seen to suppress allene formation, and the same effect may operate here. In the transition state for allene formation partial positive charge probably builds up on the β- and β′-C atoms (see **30**). This should be true for the case of carbenoid or carbene-derived transition states. An electronegative O substituent on the γ-C would be expected to retard such charge formation. All three effects (activated ε C–H, favorable carbenoid stereochemistry, O inductive effect) could be operative in diverting **27a** (and **24b** and **25b**) from the anticipated allene-forming reaction.



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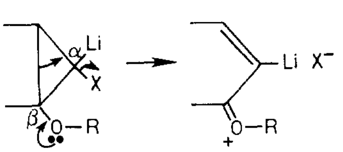
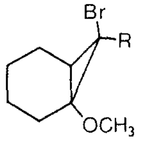
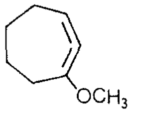


31 32

Allene formation and carbon skeleton rearrangement. If a γ-alkoxyl substituent retards allene formation by an inductive effect then a β-alkoxyl substituent (see **31**) may enhance allene formation by a resonance effect. Thus, electron donation by RO in **31** may assist in the formation of **32**, the precursor of an alkoxyallene. Precisely this type of behavior was seen in the case of the carbenoids derived from 1-methoxy-7,7-dibromo-bicyclo[4.1.0]heptane (**33a**).[18] Reaction of **33a** with ethereal MeLi gave carbenoid **33b** in high yield, as evidenced by the formation of **33c** upon quench with H_2O or D_2O. Formation of the *endo*-bromo carbenoid in this case again highlights the directing effect (kinetic and/or thermodynamic) of suitably positioned O substituents[15] on carbenoid formation. Thermolysis of **33b** gave **35** formed, for certain, by dimerization of the cyclohepta-1,2-diene **34**. No allene-derived products from numerious norcaranylidenes had been previously reported. The major reaction pathway of **16** stands in contrapoint to the present case, but a significant portion of the reaction products of **16** remain uncharacterized.[18] A similar reaction sequence (vinyl ether → alkoxy-dihalo-cyclopropane → alkoxyallene) has been adapted for the synthesis of α-, β-unsaturated aldehydes and ketones,[30] the aqueous acid hydrolysis products of alkoxyallenes. The synthesis of tetramethoxyallene was accomplished by this route.[31]



33 a R = Br
b R = Li
c R = H, or D
d R = alkyl, etc.



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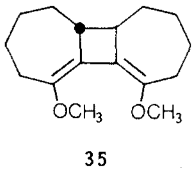

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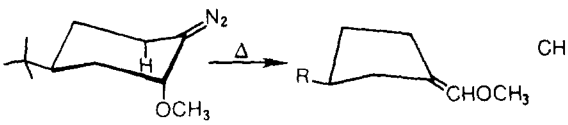
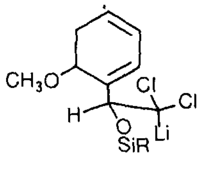
Other carbon skeleton rearrangements of carbenes and carbenoids are promoted by alkoxyl substituents. Recalling a case previously cited above for the Bamford–Stevens rearrangement,[12] Shechter has found that thermolysis of **36**, the C-2 epimer of **9**, gave a significant amount of carbon skeleton rearrangement yielding **37**, a reaction that competed with the Bamford–Stevens rearrangement of β'-axial H. Further examples from the previously cited work of Kirmse[5,10,11] illustrate the enhancement of alkyl migration to a carbene center by a β-alkoxyl substituent. Comparing **38a** and **38b**, thermolysis produced high yields of the product-types shown, with the olefins being formed *with rearranged carbon skeletons* (alkyl migration exclusively). Also, Villieras[32] has reported that the carbenoid **39** undergoes preferential α-elimination (of LiCl) accompanied by migration of the *o*-methoxyphenyl group to give, after mild acid hydrolysis, 2-chloro-2-(2-methoxyphenyl) acetaldehyde (70%). After recalling the effect of β-alkoxyl substituents in promoting H-migration in the Bamford–Stevens rearrangement, and noting these present cases, the proposal by Paquette rationalizing the enhancement by a γ-OMe substituent of carbene insertion into a δ C–H bond gains further credence.



36 **37**



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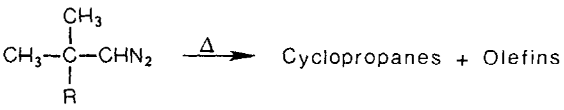
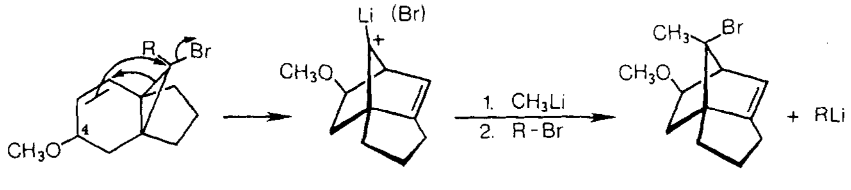


$$CH_3-\overset{CH_3}{\underset{R}{C}}-CHN_2 \xrightarrow{\Delta} \text{Cyclopropanes} + \text{Olefins}$$

	Ratios	
38 a R = C_2H_5-	75	25
b R = CH_3O-	14	86

The results of Warner[33] have implicated a carbenoid as the reactive intermediate in a "vinylcyclopropylidene to cyclopentenylidene" rearrangement.[1h] Treatment of **40a** with MeLi affords **42** as a minor, but key, reaction product. A number of experiments point to **41** as a reaction intermediate which, to yield **42**, reacts first with MeLi and then with MeBr or **40a** to give **42**. The role the 4-OMe group plays is presumably to direct the Br–Li exchange to produce **40b**. Support for this role is found in the reaction of the 4-OMe epimer of **40a** which gives lowered yields of **42** and higher yields of an alternate product.

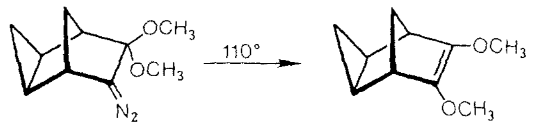


40 a R = Br
b R = Li

41

42

Alkoxyl migration. In summary thus far, alkoxyl substituents bound to ε or δ-C atoms (carbene C is α) appear to enhance C–H insertion into the respective proximate C–H bonds (late transition state; resonance stabilization). An alkoxyl substituent bound to a γ-position suppresses proximate C–H insertion (inductive affect; early transition state), suppresses the allene-forming reaction in the case of cyclopropylidenes (inductive effect) and enhances the C–H insertion reaction at C-δ ("backside" assistance). A β-alkoxyl substituent promotes β-H migration in the Bamford–Stevens rearrangement, promotes β-C migration to carbenic centers, and promotes the allene-forming reaction with cyclopropylidenes. All of the above illustrate the effect alkoxyl substituents have on adjacent atoms that react with the carbene or carbenoid center. No cases mentioned thus far are definitively interpretable in terms of a direct interaction between RO- and the carbene center, such as ylide formation. β-Alkoxyl substituents do interact directly with carbene centers, the overall result being alkoxyl group migration. However, this reaction proceeds only when optimum structural situations occur. For example Gassman has reported the thermal decompositions of **43** and **44**.[34] We can note that in the case of **43** the preferred



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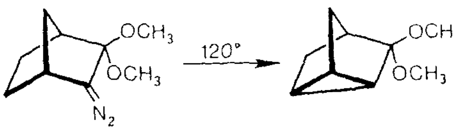

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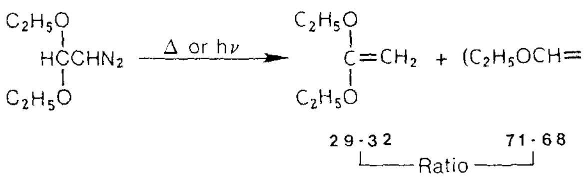

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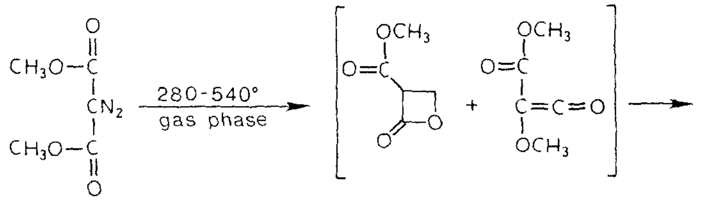
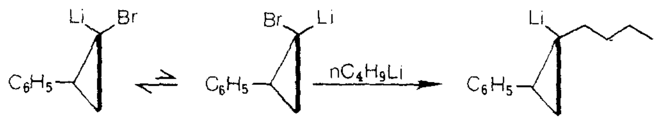


46

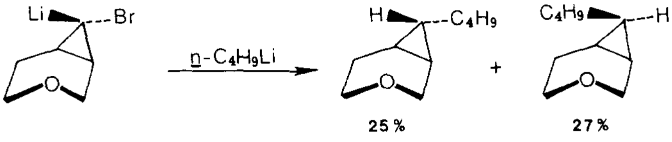
reaction of the carbene, exemplified by the reaction of **44**, is precluded by the unfavorable geometry and increased electronegativity of the C–H bond in question. From the work of Kirmse,[5] again, we note by comparing the reactions of **39** and **45**, the presence of a second alkoxyl group is required to bring the extent of alkoxyl migration to a significant level. Photolysis and thermolysis of **45** produce similar amounts of alkoxyl-migration product. With **39**, photolysis yields 0.5–1% of OMe-migration product, while thermolysis yields none. In the gas phase thermal decomposition of dimethyl diazomalonate, OMe migration (Wolff-type rearrangement) proceeds in competition with intramolecular C–H insertion.[1d] Thus, all reaction products are derived from the two reactive intermediates shown. Reference 1*d* provides a good short review of gas phase, photochemically induced Wolff rearrangements (alkoxyl migration) of alkyl diazoacetates.

The reaction of α-halooraganolithium compounds with nucleophiles (halide, R-Li) is well known. "Halogen exchange" reactions have been frequently documented in the polyhalomethyllithium series,[2,35] although such exchanges are not necessarily brought about by S_N2-type displacement reactions.[2] Recently, some work has appeared which gives some insight into the stereochemistry of the reaction of R-Li with Li carbenoids.[36] Thus, epimeric carbenoids **47** are formed by reaction in tetrahydrofuran with excess n-BuLi at −95°. The epimer **47en** reacts further at that temperature to yield **48** (which can then be treated further with electrophiles). Apparently, the phenyl group of **47** provides sufficient steric

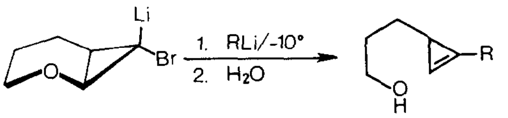


47ex 47en 48

hindrance to displacement of Br in **47ex** so that that carbenoid is stable at −95°, undergoing reaction, to give mostly **48** *via* **47en**, only upon warming. Only one other nucleophile, lithium phenylthiolate-tetramethylethylenediamine, successfully displayed Br^- (with inversion of configuration- from **47**.[36] The potential control that alkoxyl substituents can exert over carbenoid configuration and stability should provide a valuable tool for elucidating the mechanism of nucleophile displacement and exchange reactions at carbenoid centers. However, no systematic work has been done in this area and only a few observations have been recorded. Previously noted was the displacement from **25b** of chloride ion by bromide ion with inversion of configuration, and a definite dependence on Br^- for this reaction could be demonstrated,[22,23] Regarding the reaction of carbenoids with R–Li, the previously noted rearrangement of **40b** to **41**[33] was followed by reaction with MeLi to give the final, methylated, product. Thus, the Me group of **42** was derived from a nucleophilic attack by R–Li, with the Me group introduced *syn* to the OMe substituent of hypothesized intermediate **41**. Alkyllithium reagents can be brought to react with stabilized carbenoids of the n-oxabicyclo[4.1.0]heptyl series.[21,37] While the reaction of **49** with ethereal n-BuLi was not studied further,[37a] the results suggest that a non-stereospecific mechanism (perhaps carbene capture) may operate in certain situations. Finally, while the reaction of **50** with RLi imparts no stereochemical information, and the mode of incorporation of group R is unknown, the result is intriguing and of potential synthetic utility.[37b]



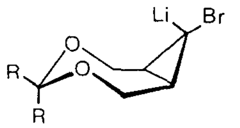
49



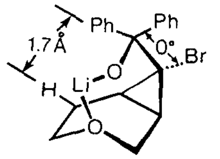
R = n-C_4H_9,
cyclopentyl-

50

Nucleophilic properties. Köbrich's[2] use of tetrahydrofuran, and solvent mixtures containing THF, to stabilize carbenoids (a solvation effect) has made a number of interesting organolithium reagents available for synthetic use as nucleophiles. A suitably located alkoxyl substituent in such a reagent can afford intramolecular solvation of the Li atom and extend the temperature range of stability of the compound.[21,22] Apart from this, an intramolecular solvating group can dramatically alter the nucleophilic properties of a carbenoid. For example, while carbenoid **49** displayed about the same thermal stability as **50** and **51**, it was *unreactive* towards benzophenone; however **50** reacted rapidly in ether at −78° while **51a** and **b** were intermediate in reactivity. The failure of **49** to react is striking when it's recalled that alkyllithium reagents react ~10^3 times faster than Grignard reagents and can be used to make hindered tertiary alcohols, e.g. tri-t-butyl carbinol.[38] If it's assumed that the Li atom of **49** remains bound to the ring O atom in the transition state of addition to benzophenone, then rather severe non-bonded



51 a R = H
b R = CH_3



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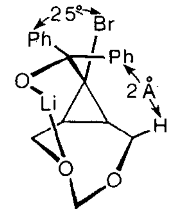
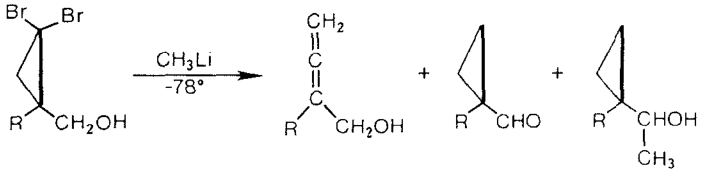


53

interactions develop, as exemplified by the structure of the adduct **52** (Drieding stereomodels). In contrast, molecular models predict a less crowded adduct, **53**, for **51** and a strain free adduct for **50**. Finally, Hiyama *et al.*[39] have used carbenoid **33b** as a starting point for the synthesis of a series of 1-substituted-cyclohept-2-enones. Treatment of **33b** with a variety of electrophiles ($(CH_3)_3SiCl$, R–CH=O, R–Br R–I) gave products **33d**. Basic methanoylsis of **33d** followed by aqueous acid treatment yielded the cycloheptanones. A similar sequence of reactions was applied to the lithium carbenoid derived from 1,1-dibromo-2-ethoxycyclopropane. These afforded a series of 1-substituted-propenals.

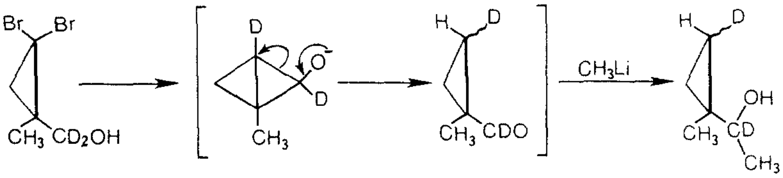
(B) *Hydroxyl or alkoxide groups*

C–H insertion and "O–H insertion" reactions. Normally, unprotected OH groups are avoided in carbene and carbenoid chemistry. However, when OH groups are present, interesting and useful chemistry often results. Skattebol[40] has reported results which indicate that a γ-alkoxide function may enhance insertion into a γ C–H bond. Treatment of alcohols **54** with excess MeLi yielded the expected allenic alcohols as major products, along with aldehydes **55** and/or the alcohols derived from reaction of **55** with MeLi. In the case of **54c**, *trans*-2-phenylcyclopropane carbaldehyde, an isomer of **55c**, was also isolated. The results suggest the presence of an unstable, bicyclo[1.1.0]butan-2-olate intermediate and further evidence for this was provided by the results using deuterated alcohol **56**. The cyclopropyl alcohol isolated had D distribution (as shown) consistent with the intermediacy of alcoholate **57**.



54 a R = H
b R = CH_3
c R = C_6H_5

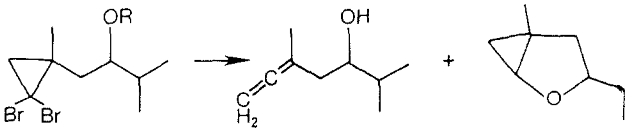
55



56

57

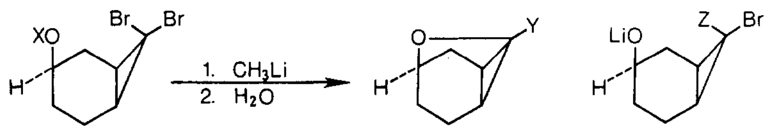
Bertrand *et al.*[44] have prepared allenic alcohols by a similar route but found it necessary to protect the OH function for optimum allene yield. Reaction of **58a** with BuLi gave the corresponding allenic alcohol (after acid treatment) in 60% yield. A variety of other alcohols were prepared by the same sequence. With **58b**, however, the allene yield was reduced to 20% by the competing formation of the corresponding debrominated cyclopropane (30%) and the bicyclic compound **59** (35%). This last product,



58 a R = $Si(CH_3)_3$
b R = H

59

formally an O–H insertion product, alternately might arise by way of nucleophilic displacement of bromide from the carbenoid. Insight into the mechanistic possibilities is provided by the work of Baird.[42] Treatment of **60a** with methyllithium in ether gave **61a** and **61b** in moderate and comparable yields. Reduction (incomplete) of **61b** with MeLi followed by an H_2O or D_2O quench gave **61a** and **61c**, respectively. A D_2O quench of a reaction of **60a** and CH_3Li however, produced no **61c** indicating that little or no **61d** was present at the end of reaction. Interestingly, deuterio alcohol **60b** gave **61c** (70% D incorporation) after MeLi treatment and H_2O quench. Thus, it may be that **61a** is in large part a product of a carbenoid insertion into an O–H bond. (Br–Li exchange using RLi competes favorably with the reaction of RLi with OH groups.[43]) Unfortunately, a pathway proceeding from initial Br–Li exchange to **62a** or **62b** followed by intramolecular displacement of bromide ion was not experimentally ruled out. Intramolecular alkoxide displacements of bromide ion on a cyclopropane ring, to give oxaspiropentane derivatives, are well known and facile.[44] Further, bromo compound **61b** could, in fact, be a product of an intramolecular displacement reaction on a carbenoid center. Conversion of **62c** to **61d** may well be facile and the product, **61d**, may well undergo Li–Br exchange with methylbromide or **60a** to give **61b** (recall the conversion of **40b** to **42** via **41**).

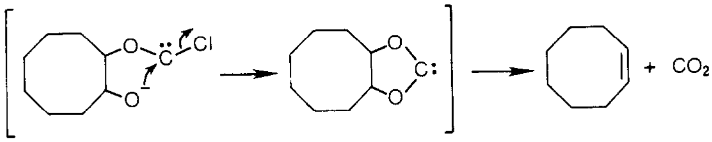


60 **a** X = H
b X = D

61 **a** Y = H
b Y = Br
c Y = D
d Y = Li

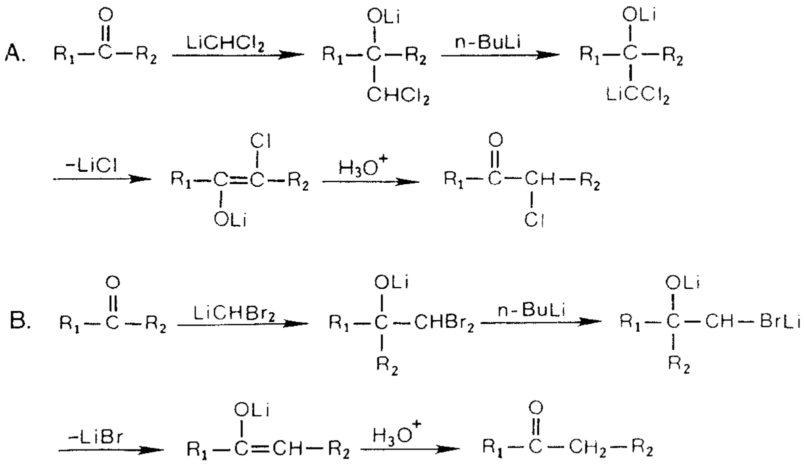
62 **a** Z = H
b Z = D
c Z = Li

An intramolecular displacement at a carbene center seems to intervene to a minor extent in the reaction of vicinal glycols with dichlorocarbene generated under phase-transfer conditions.[45] Thus, *cis*-cyclooctane-1,2-diol reacts to give cyclooctene and the dichlorocarbene adduct of cyclooctene in low yield-accompanied by other products. The pathway proposed involved intramolecular displacement of chloride ion by the neighboring alkoxide group of **63** to give the cyclic dialkoxy carbene **64**. Carbenes such as **64**, generated by other routes,[46] are known to decompose to give alkenes. Further, the conversion of *meso*-1,2-diphenylethanediol to *cis*-stilbene by this route is consistent with the intermediacy of a cyclic carbene.



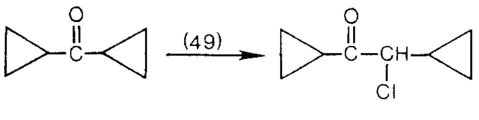
63 **64**

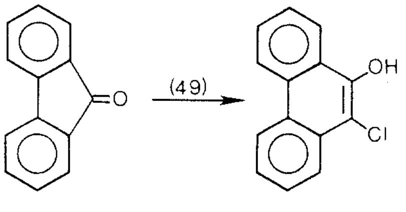
Rearrangements of β-oxido carbenoids. In 1972 Villieras[47] reported a new reaction of Li carbenoids derived from 1,1-dichloro and 1,1,1-trichloro-2-alkanols which proceeded with H- or alkyl-migration to produce α-chloro-aldehydes and ketones regiospecifically. Since that time a number of authors have published work expanding on the applications of the reaction in organic synthesis.[48–55] The overall reaction sequence begins with the reaction of a dihalomethyllithium reagent with an aldehyde or ketone, and the general schemes for dichloromethyllithium and dibromomethyllithium are shown below (Scheme 3). Operationally, the dihalomethyllithium reagents are prepared at low temperature and brought to react at low temperature with the aldehyde or ketone. That product is treated in the same pot with n-BuLi and the reaction is allowed to warm to room temperature, whereupon it's quenched with aqueous acid, and

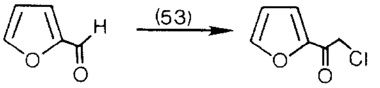


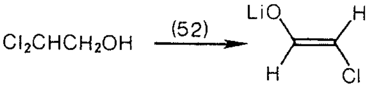
Scheme 3.

worked up. The rearrangement reaction shows excellent breadth as illustrated by the transformations below:

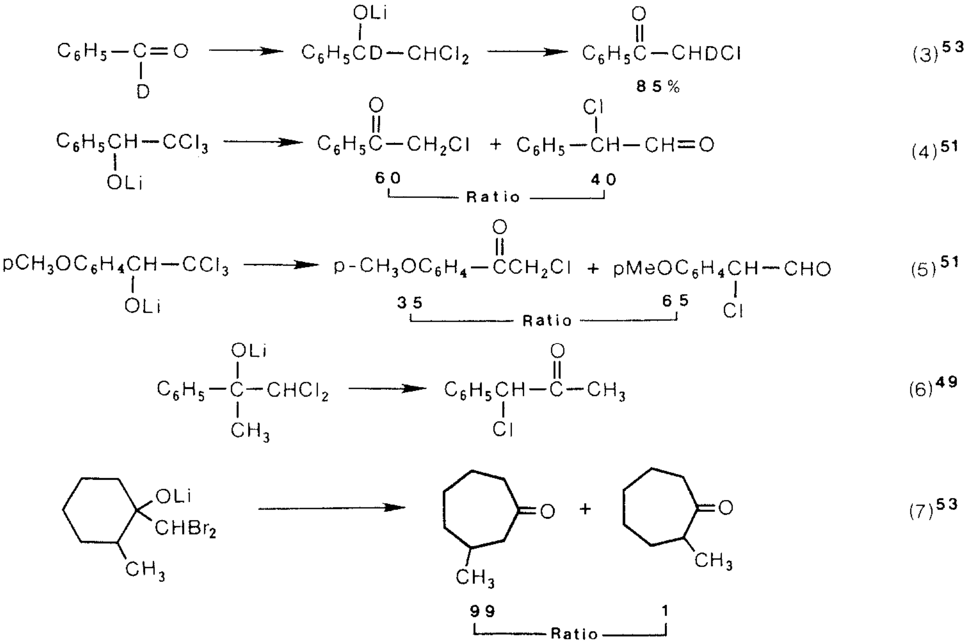






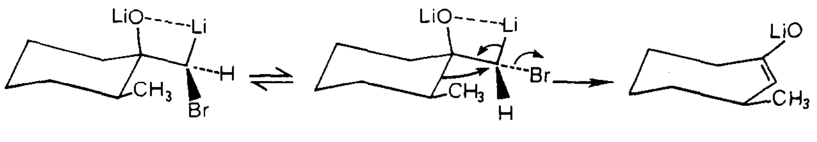


The reaction shows good regioselectivity and a rough order of "migratory aptitudes" of potential migrating groups (shown as R_2 in Scheme 3) can be gleaned from the lit: H > aryl > alkyl. Some subordering is possible within the aryl and alkyl groupings and examples of each are shown below in Scheme 4. Reaction (3) illustrates that the rearrangement involves a true hydrogen migration. Reactions (4) and (5) demonstrate that aryl migration can compete with H migration under the right conditions and



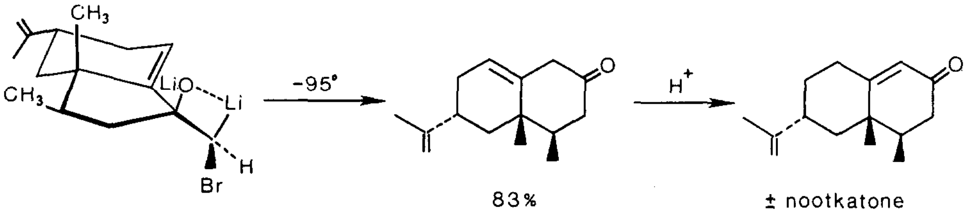
Scheme 4.

that electron donating substituents facilitate aryl group migration. Reaction (7) illustrates that excellent regioselectivity can be obtained in the competitive migration of alkyl groups with migration of the bulkier group preferred. This is interpreted[53] as a steric effect assuming, first, that equilibration can be



65 66

reached between diastereomers **65** and **66**. At equilibrium, **66** should predominate. Migration of the alkyl group *anti* to the departing bromide ion imparts the observed specificity to the reaction. This regioselectivity was recently exploited in the synthesis of racemic nootkatone.[55] Specifically, β-oxido-carbenoid **67** was generated by sequential reactions of the corresponding ketone with dibromomethyllithium and n-BuLi. Inspection of molecular models readily reveals that the preferred carbenoid configuration is that one with the Br atom *anti* to the vinyl group.



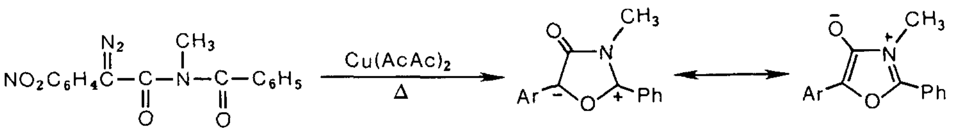
67

Finally, recent variants of the reaction sequences have permitted the synthesis of homologized α-bromo ketones,[51] the conversion of aldehydes to ketones[54] and the synthesis of α-alkylated and arylated ketones.[54]

(C) *Carbonyl groups*

α-Diazoketones: intramolecular ylide formation with, and insertion into C=O *bonds.* The synthetic aspects of intramolecular cycloadditions and C–H insertion reactions of α-diazoketones and esters have been reviewed most recently.[1c] Less recent reviews deal with intermolecular versions of those same reactions[56] and with the Wolff rearrangement[57] of α-diazo carbonyl compounds. Nestled in the above-referenced, voluminous body of chemistry are some examples of reactions of α-keto-carbenes with remote heteroatom centers. Carbonyl ylides, preparable by reaction of a carbene with a C=O group, have received some continued attention.

In 1974 Ibata[58] achieved the synthesis of a stabilized, isolable, carbonyl ylide, **68**, and demonstrated its 1,3-dipolaric properties. In a similar vein Ibata, more recently,[59] prepared the ylide **69** by decomposition of 1-(diazoacetyl)fluorenone, and trapped it *in situ* with typical dipolarophiles. The regioselectivity displayed by methyl propynoate, below, was encountered with alkenic reactants also.



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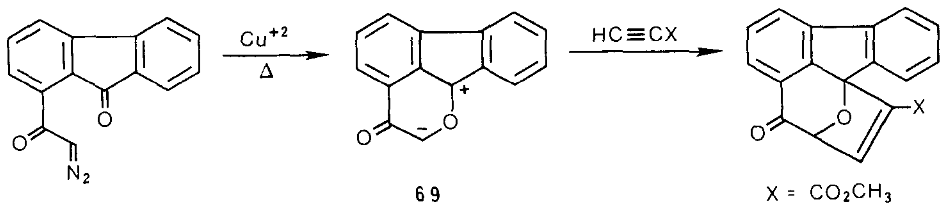
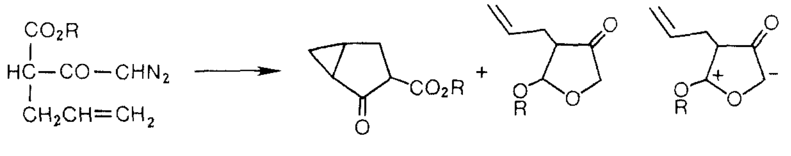


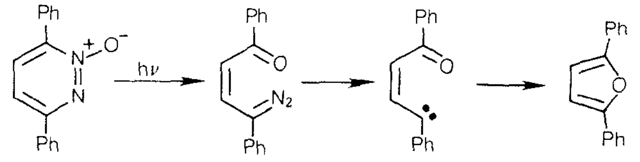
69

In the acyclic system **70**, devised by Bien,[60] competition between remote C=C and C=O groups for reaction at the carbenic center can be observed. Thus the bicyclic keto-esters are formed by cycloaddition at the C=C, whereas the (2H)-furanone results from an ylide-forming reaction (see **71**) at the ester CO group. Thermolysis of **70** favored furanone formation (54 : 15). Palladium and copper acetylacetonate-type catalysts favored keto-ester formation (*ca.* 50 : 1), while phosphite-complexed copper salts and a rhodium catalyst favored furanone formation (10–50 : 1). No predictive generalizations can be made from the catalytic reactions' results.



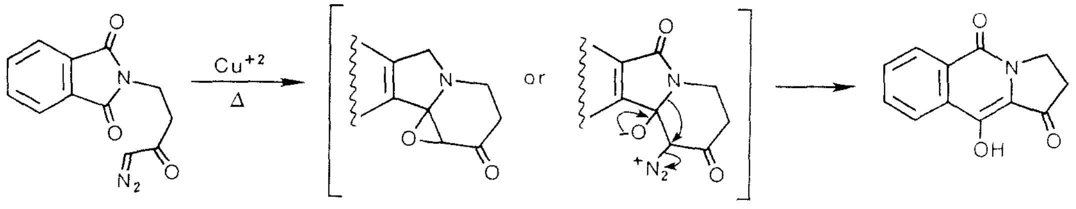
70 R = C_2H_5 71

Vinylogous diazoketones result from the photolytic decomposition of aromatic 1,2-diazine-N-oxides. Buchardt *et al.*[61] have examined the pyridazine-N-oxide system **72** in some detail. Photolysis of **72** produced the diazoketone **73**, presumably *via* an intermediate oxaziridine. Compound **73**, intensely yellow of course, was stable at −70° in solution and could be characterized spectroscopically. Further photolysis of **73** afforded 2,5-diphenylfuran in yields up to 67%. The furan product is most likely derived from a carbene and not directly from **73** since it is a photo-product. A competing thermal reaction converted **73** to 3-benzoyl-5-phenylpyrazole.



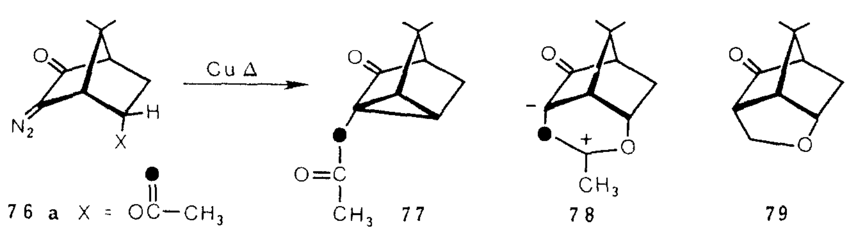
72 73

Krauser and Watterson[62] have used the intramolecular reaction of a diazoketone with an amide group to effect the enlargement of a phthalimide ring. Catalyzed thermolysis of **74** gave the diketone **75** in 25% yield. The authors pictured the cyclization step as a cycloaddition to an imide CO group. However, an "old fashioned" diazoalkane ring expansion-type reaction might be operative as well.



74 75

Yates[62] has encountered an apparent intramolecular insertion into a C=O bond which, in fact, proceeds by way of a carbonyl ylide-like intermediate. In examining the intramolecular insertion of carbenes into C–X bonds using diazoketones **76** it was found that only **76a** produced a product akin to **77** (**76b** gave **79**, **76c** gave other products). Oxygen-18 labelling of the ester CO group of **76a** established that



76 a X = $\overset{\bullet}{\overset{\|}{\mathrm{O}}}\mathrm{C{-}CH_3}$ 77 78 79

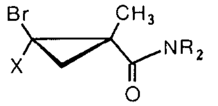
b X = $-OCH_3$

c X = Cl or Br

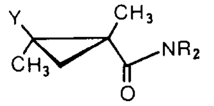
O atom became the alcohol O atom in product **77**. Thus the "insertion" reaction must have proceeded through an intermediate or transition state structurally similar to **78**.

In summary of this section it can be said that carbene centers seem to react with more facility with remote carbonyl O atoms than with remote ether O atoms. The possibility for resonance stabilization of carbonyl ylide-type intermediates or transition states may account for this difference in reactivity.

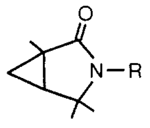
Carbenoids with neighboring C=O *groups.* Baird[63] has examined the chemistry of the Li carbenoid derived from dibromocyclopropane **80a**. The Br–Li exchange reaction of **80a** with ethereal MeLi is directed to the more hindered Br *cis* to the bulky carboxamide group (R = i-Pr), as evidenced by the formation of **80c** upon H_2O quench. The resulting carbenoid **80b** is stabilized with respect to α-elimination, but seems to display enhanced basicity. The directing of the exchange reaction and resultant stabilization must be a consequence of coordination of the Li atom by the carboxamide group and the C=O moeity seems to be the logical choice. The authors[63] report a normal amide C–N rotational barrier in **80** derivatives which indicates sp^2 hybridization at N. Such hybridization would keep the bulky R groups at maximum separation as well. While basic, **80b** in ether displays a reluctance to react with other electrophiles, even trimethylsilyl chloride and CO_2!; however, reaction with benzaldehyde occurred giving **80e**. A D_2O quench of fresh **80b** at −78° gave **80d** with only 63–70% D incorporation; and warming **80b** to room temperature (or above) gave **80c** as the product. This type of behavior of **80b** is strongly reminiscent of that of **49**[21,37a] which has an analogously placed O atom. This behavior may be due to a Li atom tightly held by intramolecular coordination, hence not readily moved as would be necessary in reaction with trimethylsilyl chloride, yet easily exchanged for a comparably sized proton. Baird and Baxter[63] attempted to characterize the reaction which gave **80c** when the carbenoid was quenched with D_2O. While the proportion of **80c** over **80d** was dramatically increased when a D_2O quench of **80b** was made after a short period at elevated temperature, **80b** aged at −60° for 30 min and quenched with D_2O showed the same D incorporation as when fresh **80b** was quenched with D_2O. Experiments with deuterated solvent identified that as a "quenching agent" but this occurred at elevated temperature. The data still point to a reaction which converts **80b** (or **80a**?) to **80c** at the time of Br–Li exchange. Of significance were the reactions of MeLi with **80c** and **80d** which gave **81** and **82** as major products as follows. Reaction of **80c** at ether reflux produced **81a** and **82** (ratio 1:8). Thus, the carbenoid, (**80b**) produced from **80a** at low temperature and then warmed (to give **80c**) behaved differently from that produced by metalation of **80c** at higher temperature. Mixing **80d** with MeLi at low temperature and allowing the mixture to reach room temperature, and complete reaction, produced **82** plus **81a** and **81b**. This last compound must arise by (C=O assisted?) displacement of Br from **80c**, while the formation of **81a** requires a second process. Little allene formation occurred, as might be expected with an electronegative group at a terminus that acquires positive charge in the transition state of allene formation.



80 a X = Br
b X = Li
c X = H
d X = D
e X = C_6H_5CHOH



81 a Y = H
b Y = D



82

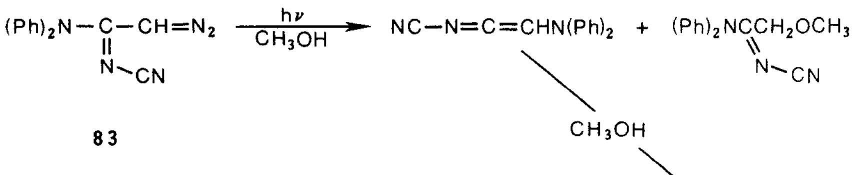
R = $\underline{i}$-C_3H_7

Skattebol[64a] and Nader[64b] have observed similar directing effects on Br–Li exchange, and similar resistance to allene formation (in favor of C–H insertion) in cyclopropyl methyl ketone and cyclopropyl carboxylic ester series.

In summary of the above, the chemistry of Baird's carboximide system-**80**, reveals a strong "substituent effect" on cyclopropyl Li carbenoids exerted by a coordinating CO group.

3. SYSTEMS WITH NEIGHBORING AMINO FUNCTIONS

Amino groups have been shown to migrate to carbenic centers in systems susceptible to Wolff-type rearrangement.[57] A recent example of this appears in the work of Regitz[65] on α-amino carbene reactions.[66] Using a new method for preparation of the required diazo compound, **83**, Regitz and Arnold found that photolysis in methanol afforded two products resulting from (1) methanol capture of the intermediate carbene, i.e. an amidine and (2) from methanol capture of an intermediate ketenimine, i.e. imidate **84**. The ketenimine generated in benzene by photolysis was also trappable by a cycloaddition reaction using benzylideneaniline. At present it's not possible to accurately predict when an amino group will migrate to a carbenic center. For example, while the carbocyclic system **85**, and others structurally related to it, undergo ring expansion to cyclobutene derivatives,[67] the corresponding aziridine system[68] does not give products derived from ring expansion reactions.



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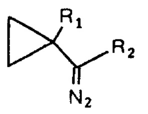

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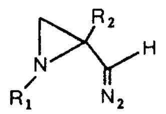

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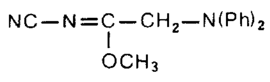
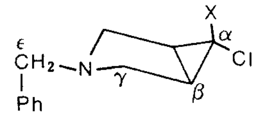
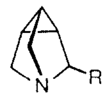


84

Two systems have been examined in which α-halo-cyclopropyllithium groups have been substituted with neighboring amine groups. Bass[69] prepared the chloro-cyclopropane **87b** by reduction of **87a** with zinc in acetic acid. Reaction of **87b** in ether with n-BuLi produced the tricyclic amine, **88a**, a product of C–H insertion at the ϵ aC–H bond. Since the C-6 epimer of **87b** failed to give **88a** on reaction with BuLi, it appears that the formation of **88a** is a stereoselective reaction of carbenoid **87c**. Direct treatment of **87a** with n-BuLi gave **88a** in low yield reflecting a lack of stereoselective Li–Cl exchange in this system, a result that parallels that previously found in the 3-oxa-bicyclo[3.1.0]hexane system.[21] When the phenyl group of **87** was replaced by a benzyl group, a similar series of reactions produced ϵ C–H insertion as well, yielding a decomposition product of **88b**.[67b]

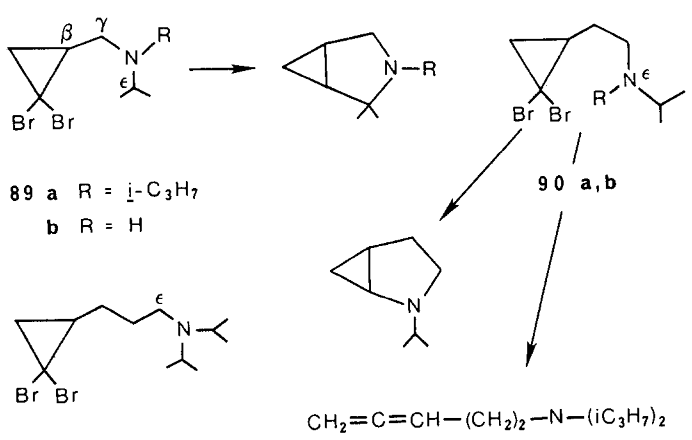


87 a X = Cl
b X = H
c X = Li



88 a R = C_6H_5
b R = $CH_2C_6H_5$

Baird[68] has examined amine analogs of his previously investigated ethers, **27**, with similar results and some additional insights into neighboring group effects. In summary, dibromocyclopropanes **89**, **90** and **91** were treated with ethereal MeLi at 25–35°. Compound **89a** gave insertion at the ϵ C–H bond giving the bicyclic amine shown, R = i-Pr, in good yield, together with a minor amount of the corresponding allene. When the N,N-dialkyl groups were changed to Et and Me, an increasing proportion of allene to C–H insertion product resulted. Compound **89b** also gave bicyclic amine *via* ϵ C–H insertion and no allene or N–H insertion occurred. When the N atom was moved to the ϵ-position, as in **90**, **90a** gave allene in good yield, while **90b** gave bicyclic amine, a product of formal insertion into the NH bond. With **91**, however, only the allene-forming reaction was observed. It appears, therefore, that when the amino group is positioned to solvate the (expected) carbenoid's Li atom in an unstrained fashion through a 5- or 6-membered ring, then insertion into an ϵ-H bond is favored. Inspection of molecular models indicates that N:Li solvation by forming a 7-membered ring, as with **91**, imparts some non-bonded, "trans-



89 a R = i-C_3H_7
b R = H

90 a,b

$CH_2{=}C{=}CH{-}(CH_2)_2{-}N{-}(iC_3H_7)_2$

91

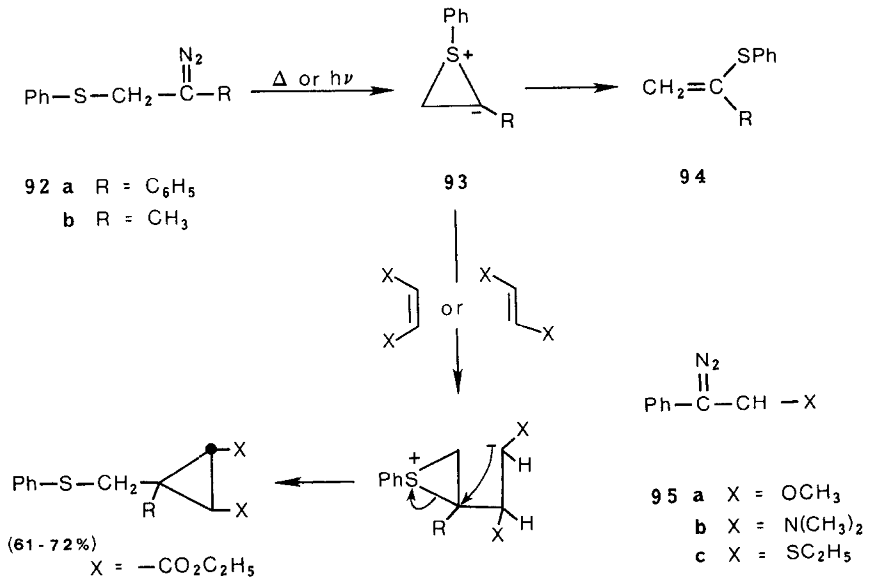
annular" repulsions that could destabilize that interaction sufficiently so as to lose the effect of N-solvation altogether.

In the main, the preceding results indicate similar behaviors for ether and amine substituents in their effects on carbenoid and carbene reactivity.

4. SYSTEMS WITH NEIGHBORING SULFUR FUNCTIONS

(A) *Thioether groups*

Carbene centers react intermolecularly with divalent S-compounds to form ylides and this behavior characterizes the intramolecular interactions of these groups. Excellent reviews emphasizing the intermolecular reactions are in print.[70] Kondo and Ojima[71–73] have made the most extensive studies of the reactions of β, γ and δ[74] arylthio- and alkylthio- substituted carbenes. These authors found that β-thioether groups underwent efficient migration to the carbenic center when the requisite diazocompounds were decomposed thermally or photochemically. Thus, **92** gave 2-phenylthio olefins **94** as the major products (ratios: 70–99) accompanied by the minor products (1-phenylthioalkenes, ratios: 1–30) which result from the Bamford–Stevens reaction. The episulfonium ylide **93** is believed to be an intermediate in these reactions and the following evidence supports that contention. Compound **92b** yields less of **94** (relative to 1-phenylthio-propene) than does **92a**. Ylide **93** can be efficiently trapped by reaction with electrophilic olefins as shown, and control experiments rule out the starting **92** as a significant reactant in the "trapping" process. The possibility for ylide intermediacy in these reactions was first proposed by Robson and Shechter[6] who discovered that in the thermal decomposition of **95**, only **95c** gave products with migration of group X. Results similar to those obtained with **92** were obtained with compounds bearing alkylthio or allylthio-substituents.[74]



92 a R = C_6H_5
b R = CH_3

93

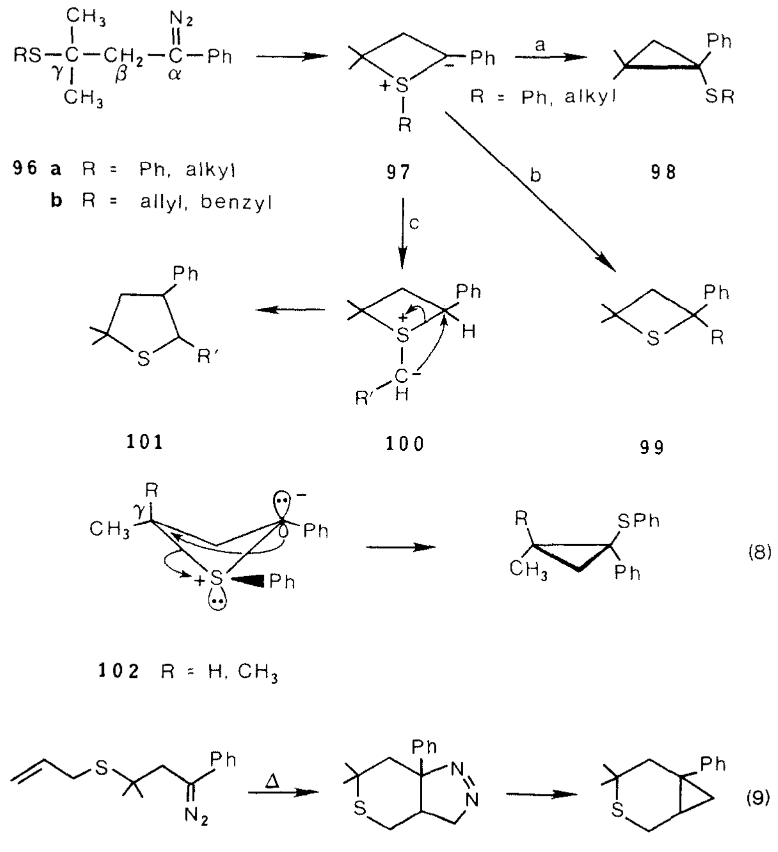
94

(61-72%)
X = $-CO_2C_2H_5$

$Ph{-}C(=N_2){-}CH{-}X$

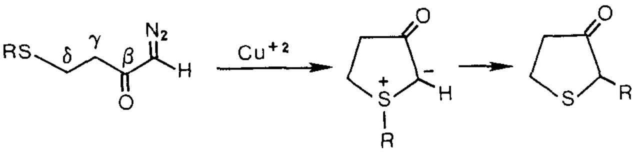
95 a X = OCH_3
b X = $N(CH_3)_2$
c X = SC_2H_5

The results of Kondo's and Ojima's studies on carbenes with γ-thioether groups[71] are summarized in Scheme 5. First, for study, diazo compounds **96a** were decomposed *thermally* and underwent the Bamford–Stevens reaction (β-H migration) to the extent of 43–77%. Also, when diazo compounds **96b** were *photolyzed* at room temperature they underwent the Bamford–Stevens reaction to the extent of 42–53%. All remaining products are derived from ylide **97** which reacts, in turn, by 3 major pathways, a, b and c. Thus, when diazoalkanes **96a** are thermolyzed the minor product-type (32–45%) was **98**. The mechanism of formation of **98** is believed to be that pictured in reaction (8), Scheme 5, and a clue to its stereochemistry was obtained in a system in which the γ carbon carried only one methyl group; i.e. **102** (R = H). In **102**, all substituents, including the non-bonding electron pairs are in their most stable conformations. Ylide **102** stereospecifically yields a cyclopropane with methyl and C-phenyl substituents *cis*. A concerted process, therefore requires inversion of configuration at the γ carbon or the carbanion carbon, and the latter mode was deemed more likely. In the photolyses of **96b**, ylide **97** was partitioned down pathways b and c. With **97b** (R = benzyl), path b essentially involved an intramolecular nucleophilic displacement of benzyl from sulfur. With **97b** (R = allyl), path b was shown to involve a [2,3]signmatropic rearrangement. Path c begins with an intramolecular H transfer to give a new ylide **100**, which in turn yields **101** by the "intramolecular displacement" mechanism shown. Thermolysis of **96b** (R = benzyl) gave results similar to those of the photolytic decomposition. Thermolysis of **96b** (R = allyl) took the alternate course shown in reaction (9), Scheme 5, giving very low yields of **99** and **101**. Thus, an intramolecular [3 + 2]-cyclization evidently intervened prior to carbene formation in this case.



Scheme 5.

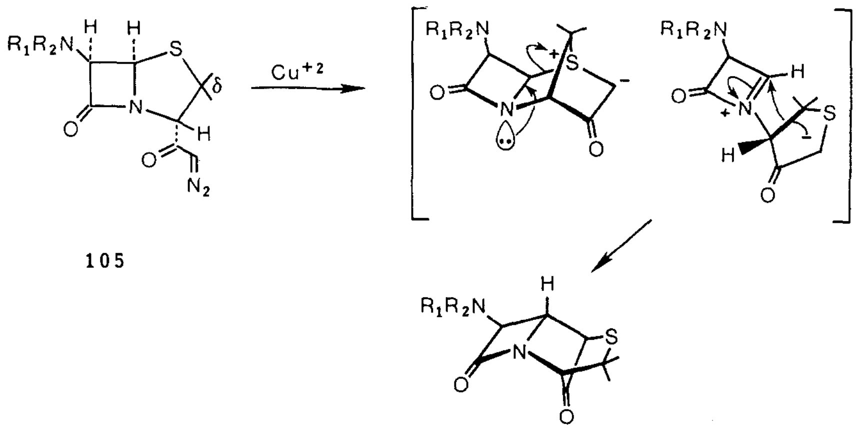
In systems with δ-thioether substituents[72] ylide formation showed stronger dependencies on structure and reaction conditions. Photolysis of **103a** in ethanol, for example, gave ethyl 4-benzylthiobutyrate, the Wolff rearrangement product, in excellent yield. In a similar system the Bamford–Stevens reaction occurred to the exclusion of ylide formation. The copper catalyzed decomposition of **103**, however, gave



103 a R = $C_6H_5CH_2-$
b R = $CH_2=CH-CH_2-$

104

thiolanones **104** in excellent yield. Similar conditions were used[75] to convert the diazoketone **105** (with a δ thioether substituent) into the tricyclic penicillin derivative **106**. The conversion probably proceeds through an intermediate ylide.

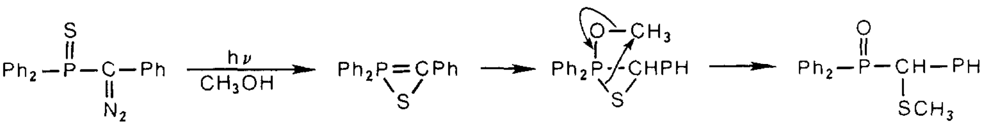


105

106

(B) *Other sulfur groups*

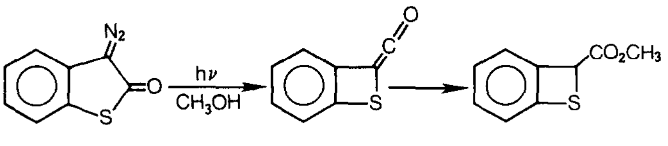
A possible example of sulfur migration from a thiophosphene moiety to a carbene center has been recently reported by Inamoto.[76] Phosphene sulfide, when irradiated in methanol, gave the phosphine oxide **108**, and a pathway through a 3-membered ring intermediate was proposed. However, it was acknowledged that thermolysis in alcohol gave no **108** while thermolysis in acidic media did give analogs



107 **108**

of **108**. Thus, the photolytic formation of **108** may involve a diazonium ion, not a carbene, intermediate.

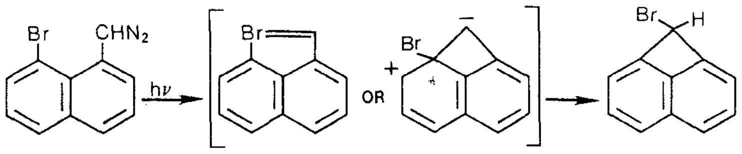
Finally, it should be noted that an α-diazo-thioester system has been shown to undergo the Wolff rearrangement with migration of S[77], a result which illustrates a better "migratory aptitude" for S than N or O in this reaction.



5. SYSTEMS WITH OTHER NEIGHBORING GROUPS

(A) *Halogen*

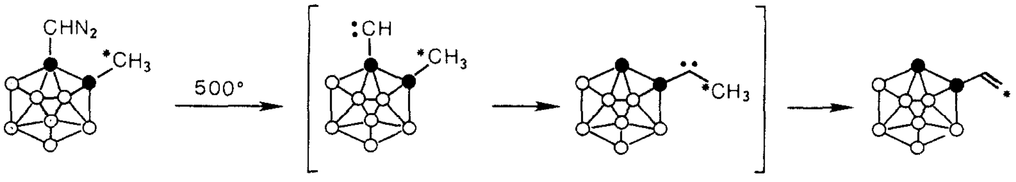
In 1974 Shechter and Bailey[78] reported the synthesis of 1,8-methanonaphthalene in which the key step was the preparation of 1,8-bromomethanonaphthalene (**109**) in 45% yield by an intramolecular carbene insertion into a C–Br bond. Recalling the negative results of Yates[62] in the norbornyl system **76c** mentioned earlier, this present result (which preceded Yates') is remarkable indeed, and may be a special mechanistic case.



109

(B) *Boron*

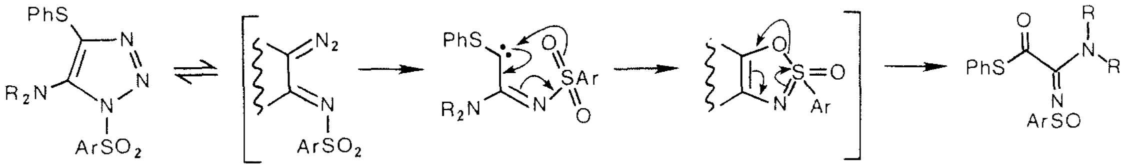
Jones *et al.*[79] have reported a carboranylcarbene rearrangement. This result which parallels other carbene–carbene rearrangements;[1f,g] however the system is a rather unusual one. Flow pyrolysis of carborane **110** *in vacuo* gave the vinylcarborane **111** in about 10% yield. The ^{13}C labelling result is consistent with the mechanism shown.



110 **111**

(C) *Sulfonimine*

A carbene is believed to be an intermediate in an unusual intramolecular redox reaction involving an oxygen transfer from S to C.[80] The 1,2,3-trizole **112**, formed by the room temperature cycloaddition of arylsulfonylazides to N,N-dimethyl-(2-ethylthio)ethynylamine, is apparently unstable and slowly evolves nitrogen with the formation of the thioester derivative **113**.



112 R = C_2H_5 **113**

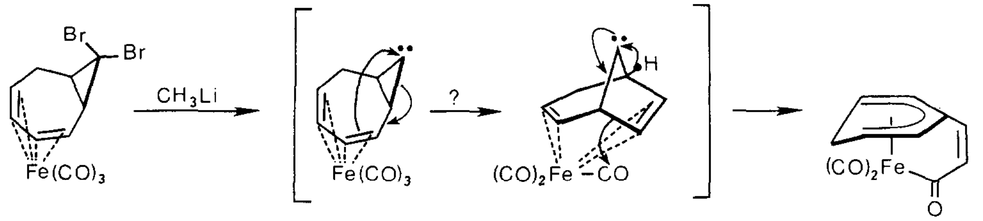
(D) *Carbanion*

Treatment of bis-dithioacetal **114** with excess MeLi afforded the cyclobutene derivative **115** in rather good yield. Experiments ruled out a direct intramolecular displacement reaction in the ring closure step. Alternatively, the dianion of **114** is believed to suffer α-elimination of thiophenoxide followed by rapid intramolecular carbanion attack on the resulting carbene. β-Elimination of the second thiophenoxide completes the conversion to **115**.

114 **115**

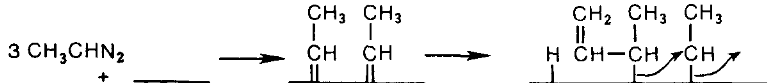
(E) *Organometallic moieties*

The transformation of reaction (10)[82] was sufficiently unusual to warrant a crystal structure determination to confirm the structure of the starting dibromide. The mechanism of the transformation is not known but the intervention of the vinylcyclopropylidene-cyclopentenylidene rearrangement would bring a 2-carbon unit within reacting distance of the iron carbonyl moiety.



(10)

Gold colloids and a variety of metal films deposited by evaporation polymerize diazomethane and diazoethane, the latter to a mixture of amorphous and stereoregular polyethylidene.[83] The mechanism is thought to involve interaction of adjacent metal carbenoid species on the metal surface (11).



(11)

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