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Synthetic Approaches to Bicyclic Diazenium Salts

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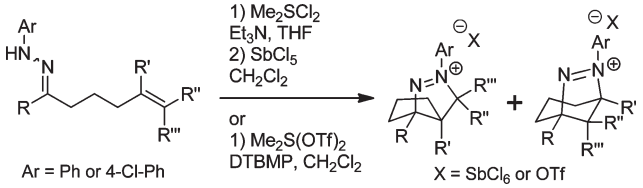
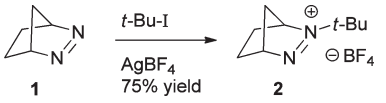


Bicyclic diazenium salts have been prepared from α-chloroazo species via a Lewis acid-mediated intramolecular cycloaddition. An alternative, more direct, route to these salts by the reaction of hydrazones with dimethylsulfonium ditriflate is also described. Terminal olefins provided mixtures of fused and bridged bicyclic diazenium salts. The ratio of the fused and bridged species was observed to depend on the electronics of the N-aryl substituent, which is explained by considering a concerted asynchronous cycloaddition mechanism.

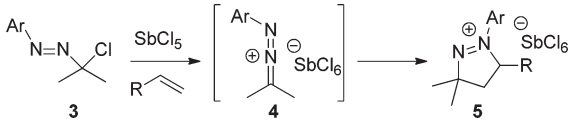
Introduction

Cyclic trisubstituted diazenium salts (e.g., **2**, Scheme 1) are cationic heterocycles that contain a reactive nitrogen−nitrogen double bond.[1] Although these species are potentially useful synthetic intermediates, they have received less attention from the synthetic community than most classes of nitrogen-containing heterocycles and few methods exist for their preparation. Nelsen and co-workers[2−5] have prepared bridged bicyclic diazenium salts by alkylation of the corresponding diazene (Scheme 1), and have studied the redox properties, structure, and charge distribution of these salts; Nelsen and co-workers also observed that protonated bicyclic azo compounds act as dienophiles in [4 + 2] cycloaddition reactions.[6,7]

SCHEME 1. Nelsen's Preparation of Bridged Bicyclic Diazenium Salts



SCHEME 2. Jochims' Preparation of Diazenium Salts



More recently, Jochims and colleagues[8−10] reported that α-chloroazo compounds (e.g., **3**, Scheme 2) react with halophilic Lewis acids to provide 1-aza-2-azoniaallene cation intermediates (e.g., **4**), which display reactivity reminiscent of Huisgen-type 1,3-dipolar compounds[11] and undergo intermolecular [3 + 2] cycloaddition with alkenes to provide diazenium salt heterocycles (e.g., **5**). We recently reported the preparation of more structurally complex bicyclic diazenium salts by rendering this Lewis acid-mediated process intramolecular.[12] The success of this intramolecular cycloaddition

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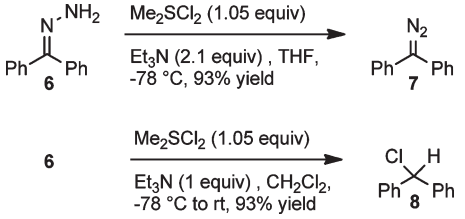
in providing structurally complex heterocyclic products from simple starting materials encouraged us to explore the formation of bicyclic diazenium salts further and we present our results here. We also report our discovery that bicyclic diazenium salts can be formed directly from hydrazones by reaction with dimethylsulfonium ditriflate.

Results and Discussion

Reactions of Hydrazones with Sulfonium Salts. The work described herein stems from our recent studies on reactions of hydrazones with sulfonium salts, which we have discovered can provide a variety of useful products. For example, we have observed that unsubstituted hydrazones react readily at low temperature with chlorodimethylsulfonium chloride (Me_2SCl_2) in the presence of 2 equiv of triethylamine to provide diazo products (Scheme 3).[13,14] This method of forming diazo compounds is more environmentally friendly than the well-established dehydrogenation procedures mediated by lead or mercury salts,[15−18] and it is particularly useful for the formation of aryl diazomethanes. Unstabilized aliphatic diazo compounds appear to form readily under these reaction conditions, but these more reactive species are unstable in the presence of the triethylammonium chloride that is generated over the course of the reaction.

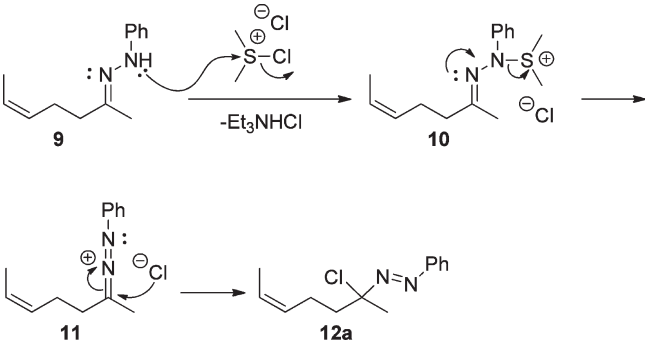
SCHEME 3. Sulfonium Salt-Mediated Formation of Diazos and Alkyl Chlorides



Changing the reaction conditions so that equimolar quantities of triethylamine and hydrazone are used in the reaction results in the formation of alkyl chloride products rather than diazo species (Scheme 3).[19] This latter transformation is unique in that the hydrazone starting material undergoes a net reduction under standard oxidizing conditions.

Aryl-substituted hydrazones (e.g., **9**, Scheme 4), on the other hand, reacted with Me_2SCl_2 to provide α-chloroazo products[20] (e.g., **12a**). This transformation is general and we were pleased to find that Me_2SCl_2 smoothly converted hydrazones containing a pendent alkene into the corresponding α-chloroazo species with no modification of the olefin. α-Chloroazo compounds had been prepared previously by reacting substituted hydrazones with either chlorine gas or *tert*-butyl hypochlorite,[21,22] and these products are useful synthetic precursors to azoalkenes,[23] tetrahydropyridazines,[23] 1,2,4-triazolium salts,[24,25] *N*-(azoalkyl)iminium salts,[26] 1,2,4,5-tetrazinium salts,[26] 1*H*-pyrazolium salts,[9] diazenium salts,[9] and pyrazoles.[9]

SCHEME 4. Proposed Mechanism of α-Chloroazo Formation



We hypothesize that Me_2SCl_2 reacts with hydrazones to provide α-chloroazo products by the mechanism shown in Scheme 4. Nucleophilic attack of the hydrazone on the electrophilic sulfonium salt would provide azasulfonium salt **10** after deprotonation with Et_3N. Lone pair donation by the α-nitrogen would result in elimination of dimethyl sulfide to provide the cationic heteroallene **11**, which could in turn be captured by the chloride counterion to provide α-chloroazo **12a**.[27]

Lewis Acid-Mediated Diazenium Salt Formation. With a convenient route to aryl-α-chloroazo alkenes in hand, we have begun to study the formation of bicyclic diazenium salts via intramolecular Lewis acid-mediated cycloaddition.[12] For example, treating phenyl-α-chloroazo **12a** with antimony pentachloride resulted in an intramolecular cycloaddition to provide fused bicyclic diazenium salt **13a** as a single diastereomer in 88% isolated yield (entry 1, Table 1). This transformation efficiently builds structural complexity and over the course of the reaction new carbocyclic and new heterocyclic rings form. The diastereoselectivity of this reaction further supports the notion that the cycloaddition occurs by a concerted process.[8] To assess the scope of this intramolecular cycloaddition reaction we prepared phenyl-α-chloroazo compounds **12a**−**g** (Table 1) and subjected these to the Lewis acid-mediated cyclization. Most of these substrates reacted smoothly to provide the diazenium salt products in good to excellent yield after purification by trituration from diethyl ether. Of note, electron-deficient alkene **12c** reacted with $SbCl_5$ to provide the desired diazenium salt **13c** (entry 3, Table 1) in 83% yield. This result is significant because electron-deficient alkenes do not participate in intermolecular cyclizations of this type[8] and this result broadens the useful substrate range of this

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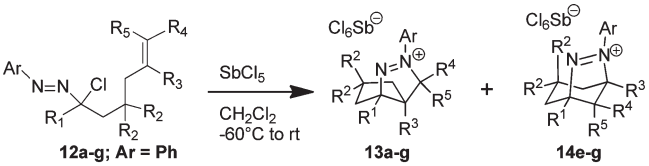
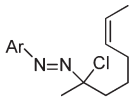
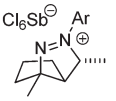
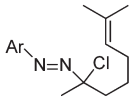
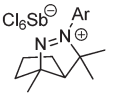
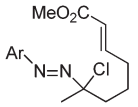
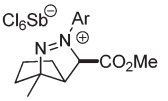
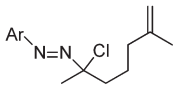
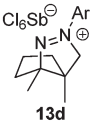
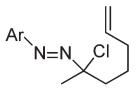
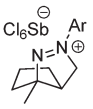
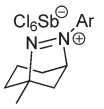
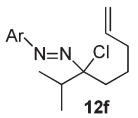
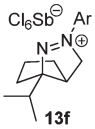
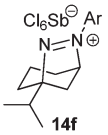
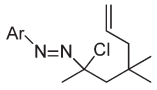
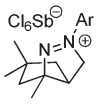
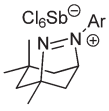
(27) Alternatively, the chloride ion could react directly with azasulfonium salt **10** by an SN_2' mechanism.

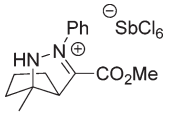
TABLE 1. Results of Intramolecular Lewis Acid-Mediated Diazenium Salt Formation



Entry	α-chloroazo	Product	Yield Ratio **13**:**14**[a]	
1				
	12a	**13a**[b]	88%	---
	12a'	**13a'**	87%	---
2				
	12b	**13b**	71%	---
	12b'	**13b'**	---[c]	---
3				
	12c	**13c**[b]	83%	---
	12c'	**13c'**	69%[d]	---
4				
	12d	**13d**	0%	---
5		 		
	12e	**13e**	**14e**	87% 1: 0.2
	12e'	**13e'**	**14e'**	92% 1: 0.3
6		 		
	12f	**13f**	**14f**	88% 1 : 0.05
	12f'	**13f'**	**14f'**	80% 1 : 0.1
7		 		
	12g	**13g**	**14g**	75% 1: 0.1
	12g'	**13g'**	**14g'**	89% 1: 0.2

[a]Diazenium salts **13g'**−**g**/**e'**−**g'** and **14e**−**g**/**e'**−**g'** were isolated as mixtures. [b]Diazenium salts **13a** and **13c** were formed as single diastereomers and their relative configurations were assigned by nOe experiments. [c]Product was formed as an intractable mixture. [d]After titration the only observable product was the minimum tautomer.

transformation. On handling, diazenium salt **13c** readily tautomerized to hydrazonium salt **15**. Disubstituted terminal alkene **12d** did not provide any of the expected diazenium salt product. In this case, the expected product would contain adjacent quaternary centers and steric encumbrance may inhibit cyclization.



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Terminal alkene **12e** reacted with $SbCl_5$ to provide a mixture of ring-fused diazenium salt **13e** and bridged diazenium salt **14e** in a 1 to 0.2 ratio (entry 5, Table 1). Mixtures of bridged and fused bicyclic diazenium salts were obtained for other terminal alkenes as well (entries 6 and 7) and the ratio of these products appears to be affected by steric factors. For example, Lewis acid-induced cyclization of isopropyl derivative **12f** provided a 1 to 0.05 ratio of fused (**13f**) to bridged (**14f**) products, while incorporation of a gem-dimethyl group within the chain (**12g**) provided the fused (**13g**) and bridged (**14g**) products in a 1 to 0.1 ratio. Formation of the fused and bridged products can be explained by considering two alternative orientations by which the alkene can approach the heteroallene intermediate. These alternate approaches would lead to transition states **16** and **17** shown in Figure 1, which would in turn provide the fused and bridged bicyclic products, respectively.

To more fully explore the scope of this transformation we prepared the 4-chlorophenyl-α-chloroazo compounds **12a′**−**g′** (Table 1) and subjected these to Lewis acid-mediated intramolecular cycloaddition as well. Modification of the aryl substituent from phenyl to 4-chlorophenyl had little effect on the outcome of this reaction and the corresponding diazenium salts **13a′**,**c′**,**e′**−**g′** and **14e′**−**g′** were formed in good to excellent yield. For reasons we do not fully understand, reactions of trisubstituted alkene **12b′** consistently provided complex mixtures that were intractable and could not be resolved to pure diazenium salt **13b′**. Another notable effect of this modification was that the terminal alkene substrates **12e′**−**g′** reacted to provide bridged and fused products in different ratios than was observed for the corresponding phenyl derivatives. In each case, the 4-chlorophenyl substrates provided a modest increase in the relative proportion of the 6,5-bridged diazenium salt product.

To further assess how the electronics of the aryl ring affect the outcome of the cycloaddition reaction, we prepared the aryl-α-chloroazo compounds shown in Table 2 and subjected these compounds to Lewis acid-mediated intramolecular cycloaddition. The ratio of the fused to bridged bicyclic diazenium salt products was determined by proton NMR analysis of the crude reaction mixtures. From these results, it is clear that the electronic nature of the aromatic ring substituent on nitrogen affects the reaction outcome; an increase in the electron-withdrawing character of the aryl ring resulted in an increase in the proportion of the 6,5-bridged bicyclic product that was formed. Conversely, a more electron-rich aryl ring provided the 5,5-fused product to an even greater extent (Table 2). A Hammett plot of these results (Figure 2) shows a linear correlation between the ratio of the products formed and the Hammett constants for the aryl ring substituents.[28−30]

(28) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96.
(29) Hammett, L. P. *Chem. Rev.* **1935**, *17*, 125.

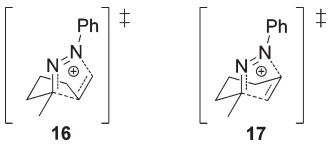
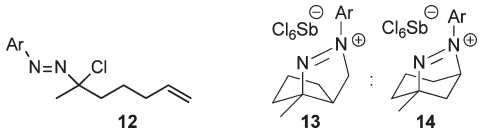


FIGURE 1. Proposed transition states leading to diazenium salts **13** and **14**.

TABLE 2. Dependence of Product Ratio on the Electronics of Aryl Substituent



Ar substituent	product ratio[a]
12e	1 : 0.2 (13e : 14e)
12e'	1 : 0.3 (13e' : 14e')
12h'	1 : 0.8 (13h' : 14h')
12i'	1 : 0.1 (13i' : 14i')

[a]Product ratio determined by proton NMR of the crude reaction mixture..

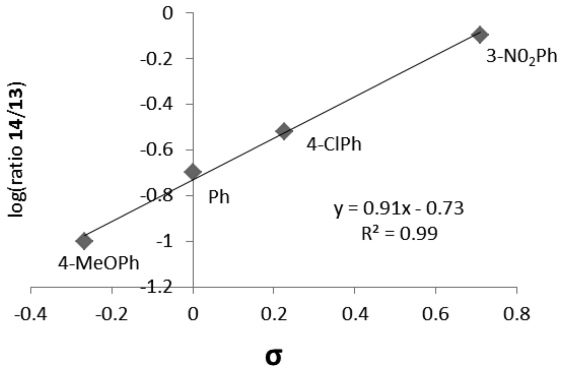


FIGURE 2. Hammett plot of log(ratio **14/13**) data vs σ for reaction of **12e**, **12e′**, **12h′**, and **12i′**.

The observation that the electronics of the hydrazone aryl substituent biases the product distribution is consistent with a concerted but asynchronous mechanism in which C−C bond formation to the highly electrophilic carbon atom of heteroallene **18** (Figure 3) is more advanced at the transition state than N−C bond formation to the heteroallene nitrogen.[10,31] If this is the case, then on route to the transition state a partial positive charge would build on the carbon

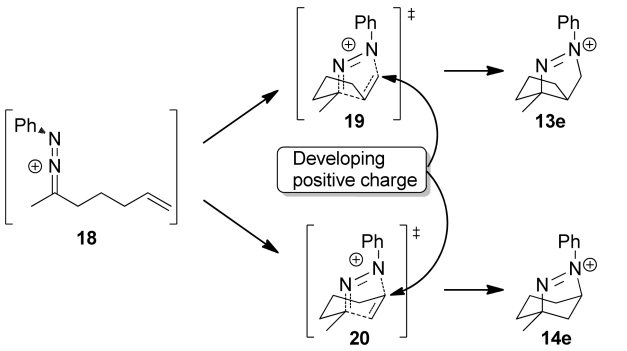


FIGURE 3. Location of charge in the asynchronous cycloaddition mechanism.

atom that forms a new bond with nitrogen. Transition state **20** (Figure 3), leading to the 6,5-bridged product **14e**, would have a partial positive charge develop on a secondary carbon atom, whereas proposed transition state **19**, leading to the 5,5-fused product **13e**, would have a partial positive charge develop on a primary carbon. While cationic charge buildup on a primary carbon would make transition state **19** higher in energy, we suspect that this transition state is entropically favored, which explains why the fused diazenium salt **13e** is always the dominant species formed (Tables 1 and 2). However, as the aryl substituent becomes more electron withdrawing, C−N bond formation should be further delayed and the amount of partial positive charge developed at the transition state would increase. If this is the case, then the amount of bridged diazenium salt (**14**) formed would be expected to increase as the aryl ring becomes more electron withdrawing, which is consistent with our observations (Table 2). In the case of terminal dimethyl substrate **12b′** (Table 1), a more stepwise process resulting in the formation of a tertiary carbocation intermediate could explain the observed formation of complex product mixtures.[31]

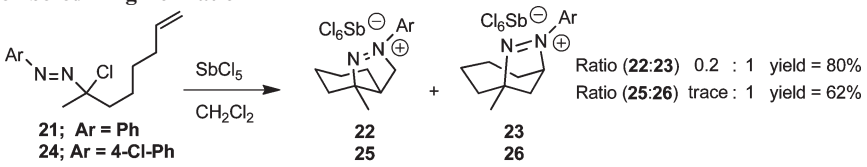
Subjecting α-chloroazo substrate **21** (Scheme 5) to intramolecular cyclization could provide either 6,5-fused (**22**) or 7,5-bridged (**23**) bicyclic diazenium salts. In this case, formation of the seven-membered carbocyclic ring was favored over formation of the six-membered ring; the 7,5-bridged diazenium salt **23** was formed as the major product in a 1 to 0.2 ratio with the 6,5-fused system. This result is important because methods to prepare carbocyclic 7-membered rings are generally lacking. As would be expected, changing the aryl ring to the more electron-withdrawing 4-chlorophenyl derivative increased the relative proportion of the 7,5-bridged product (**26**), and in this case only traces of the 6,5-fused product were observed.

Preferential formation of the 7,5-bridged products (**23** or **26**) is likely due to the fact that the reactive orbitals of the 1-aza-2-azoniaallene intermediate (i.e., the heteroallene and the alkene) cannot productively overlap to form the 6,5-fused product (**22** or **25**) when the heteroallene adopts a conformation in which the 6-membered ring that forms is in a chairlike conformation (e.g., **27**, Figure 4). To obtain reasonable orbital overlap leading to the 6,5-fused products, the 1-aza-2-azoniaallene intermediate would need to adopt an unfavorable conformation in which the 6-membered ring that forms is in a boat-like conformation (e.g., **28**). The longer tether length seems to provide sufficient flexibility in the system to allow the reacting centers to align in a conformation

(30) The log of the ratio of products obtained was used for these plots because (assuming the reaction is irreversible under the reaction conditions) these values are directly related to the free energy difference between the regioisomeric transition states. This relationship is analogus to using log(er) for Hammett plots of results obtained for enantioselective reactions. For an example of the use of log(er) in Hammett plots see: Constantine, R. N.; Kim, N.; Bunt, R. C. *Org. Lett.* **2003**, *5*, 2279.

(31) Wei, M. J.; Fang, D. C.; Liu, R. Z. *J. Org. Chem.* **2002**, *67*, 7432.

SCHEME 5. Seven-Membered Ring Formation



(e.g., **29**) leading to the formation of the seven-membered ring carbocycle without major energetic penalties. In addition, as discussed above, an asynchronous concerted mechanism would also favor the formation of 7,5-bridged bicyclic products **23** and **26**.

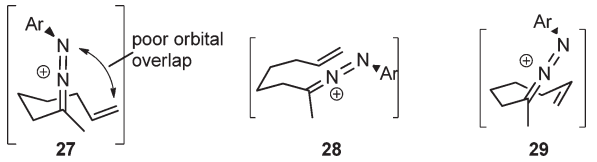
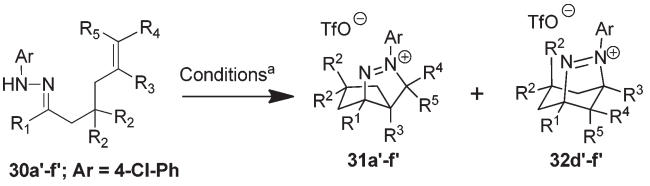


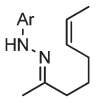
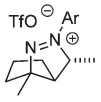
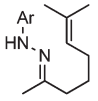
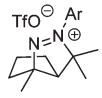
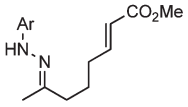
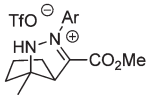
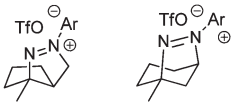
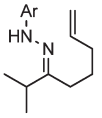
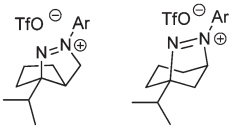
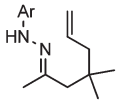
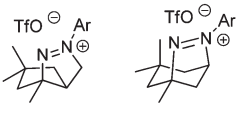
FIGURE 4. Proposed conformations leading to observed products.

Sulfonium Salt-Mediated Conversion of Hydrazones to Diazenium Salts. The mechanism we propose in Scheme 4 for Me_2SCl_2-mediated α-chloroazo formation invokes a 1-aza-2-azoniallene salt intermediate (**11**), which is subsequently captured by a chloride counterion. With this in mind, we hypothesized that a sulfonium salt bearing a non-nucleophilic counterion might react with aryl hydrazones to provide heteroallene intermediates that could then undergo intramolecular cycloadditions to provide diazenium salt products. In this way, hydrazones would be directly converted into diazenium salts avoiding the need to prepare and isolate α-chloroazo compounds as intermediates.

Dimethyl sulfide ditriflate ($Me_2S(OTf)_2$) seemed a logical sulfonium salt to use for this transformation; it is known to have similar reactivity to Me_2SCl_2,[32] but has a poorly nucleophilic counterion that we thought unlikely to capture the heteroallene intermediate. Upon treating hydrazone **30e′** (Table 3, entry 4) with $Me_2S(OTf)_2$ and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), we were pleased to observe that the expected fused and bridged bicyclic diazenium salts (**31e′** and **32e′**) were indeed present in the proton NMR spectrum of the crude reaction mixture, along with small quantities of what appeared to be an aryldimethyl sulfonium salt presumably formed by electrophilic aromatic substitution.[33] In an effort to optimize this transformation, sulfonium salts derived by activation of dimethyl sulfoxide with acetic anhydride, trifluoroacetic anhydride, or sulfur trioxide/pyridine complex were tested for their ability to facilitate diazenium salt formation. Unfortunately, none of these activated DMSO species provided any of the diazenium salt products. Substituting pyridine, proton sponge, or 2,6-dichloropyridine as base in place of DTBMP provided notably less product, and deprotonating the hydrazone with *n*-butyllithium prior to adding $Me_2S(OTf_2)$ also failed to provide the desired product. Interestingly, a small amount of diazenium salt formed when no external base was added; in this case it seems likely that another equivalent of hydrazone starting material could be acting as base to facilitate the transformation.

TABLE 3. Results of $Me_2S(OTf)_2$-Mediated Diazenium Salt Formation[a]



Entry	Hydrazone	Product	Yield[b]	Ratio **30**:**31**[c]
1	 **30a'**	 **31a'**	61%	---
2	 **30b'**	 **31b'**	---%[d]	---
3	 **30c'**	 **31c'**	44%	---
4	 **30e'**	 **31e'** **32e'**	67%	1: 0.4
5	 **30f'**	 **31f'** **32f'**	66%	1 : 0.1
6	 **30g'**	 **31g'** **32g'**	54%	1: 0.2

[a]Conditions: $Me_2S(OTf)_2$ (1.1 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (1.2 equiv) CH_2Cl_2 (0.02 M), −78 °C (20 min), −78 °C to rt (35−40 min), added benzyl ether (0.5 equiv), solvent removed in vacuo. [b]Yield determined by NMR vs an internal standard. [c]Diazenium salts **31e'**−**g'** and **32e'**−**g'** were formed as mixtures. [d]Product formed in low yield as an intractable mixture.

(32) Hendrickson, J. B.; Schwartzman, S. M. *Tetrahedron Lett.* **1975**, *16*, 273.

(33) Nenajdenko, V. G.; Vertelezkij, P. V.; Balenkova, E. S. *Sulfur Lett.* **1996**, *20*, 75.

To check the reaction time, several reactions were allowed to proceed at low temperature (−78 °C) for prolonged periods (up to 48 h). These runs led to inconsistent results; reaction time did not correlate to reaction outcome, which indicated to us that reaction temperature might be an important parameter. To better understand temperature effects on the course of the reaction we monitored the processes by variable-temperature NMR. When a −78 °C solution of the hydrazone and DTBMP in CD_2Cl_2 was added to a −78 °C solution of $Me_2S(OTf_2)$ in CD_2Cl_2, a significant change in the proton NMR signals of the hydrazone occurred, indicating that a reaction had occurred between these two compounds. However, at this low temperature no diazenium salt product was observed to form. The temperature of the NMR probe was raised by 10 °C increments and spectra were recorded at each stop along the way. Raising the temperature caused no change in the spectrum until the temperature reached −40 °C, at which point traces of diazenium salt appeared. Increasing the temperature to −30 °C provided only slightly more diazenium salt. However, a critical temperature was reached between −30 and −20 °C, and the reaction proceeded to completion over this temperature range; no changes were noted in the spectrum above −20 °C. On the basis of these data, we hypothesize that $Me_2S(OTf_2)$ reacts rapidly with the hydrazone at low temperature to provide an aza-sulfonium intermediate (e.g., **10**, Scheme 4) that appears to be stable until the temperature is increased above −30 °C. At this higher temperature, formation of the heteroallene and subsequent intramolecular cycloaddition with the alkene would provide the diazenium salt products. With these data in mind, it is not surprising that allowing the −78 °C reaction mixture to warm to room temperature 20 min after mixing the reagents consistently provided cleaner products and this became the procedure of choice.

To determine the scope of this one-step diazenium salt-forming reaction, hydrazones **30a′**−**g′** were subjected to the reaction conditions and the results from these studies are shown in Table 3. The diazenium salt products (**31a′**−**g′** and **32e′**−**g′**) formed in these reactions are highly polar and labile compounds and our attempts to purify these products from the reaction mixtures have not yet been fruitful; all standard purification techniques (e.g., extraction, chromatography, HPLC, ion exchange chromatography) failed to return clean product. However, the NMR spectra of compounds **13a′**−**g′**·$SbCl_6$ and **14e′**−**g′**·$SbCl_6$ (Table 1) were identical to those of the triflate salts shown in Table 3 and thus identifying the desired products in the product mixtures was trivial. Yields for these transformations were established by integration of the NMR spectra by adding a known quantity of benzyl ether to the reaction mixture to serve as an internal standard.

Treating hydrazone **30a′** with $Me_2S(OTf_2)$ and DTBMP provided diazenium salt **31a′** in 61% yield. Only a single diastereomer of **31a′** was observed and the diastereoselectivity of this process is consistent with the selectivity observed for the $SbCl_5$-mediated reaction, which supports the notation that the $Me_2S(OTf_2)$-mediated reaction also proceeds through a heteroallene intermediate.

Hydrazone **30b′**, which has a pendent trisubstituted olefin, provided diazenium salt **31b′** as a complex mixture in less than 30% yield. The low yield in this case is not surprising in view of the poor results obtained for the corresponding Lewis acid-mediated cyclization of α-chloroazo **12b′**. Hydrazone **30c′**, bearing a pendant enoate, was also a competent reactant and after trituration returned iminium ion **31c′** in 44% yield. As noted earlier, iminium ion **31c′** results from isomerization of the corresponding diazenium salt.

Hydrazones **30e′**−**g′**, each bearing a terminal olefin, all reacted with $Me_2S(OTf_2)$ to provide mixtures of fused and bridged bicyclic diazenium salts in 67%, 66%, and 54% yield, respectively. In each case, the ratio of bridged to fused product is comparable to the ratio obtained by the Lewis acid-mediated cycloaddition, which again supports our supposition that these two transformations occur via a common heteroallene intermediate.

Conclusions

The studies described here indicate that reactions between hydrazones and sulfonium salts are versatile and useful for the preparation of a variety of products. Unsubstituted hydrazones react efficiently at low temperature with Me_2SOCl_2 to provide either alkyl chlorides or diazo compounds depending on the quantity of base present, whereas aryl-substituted hydrazones react with Me_2SOCl_2 to provide α-chloroazo compounds in good yield. Importantly, when aryl-substituted hydrazones that contain a pendent alkene are converted into α-chloroazo compounds the olefin is untouched and these products readily participate in Lewis acid-mediated intramolecular cycloadditions to provide bicyclic diazenium salt products. Our data support the supposition that this cycloaddition occurs by a concerted[8] but asynchronous mechanism. Aryl hydrazones that bear a pendent alkene could be directly converted into diazenium salt products by reaction with $Me_2S(OTf_2)$. These latter transformations result in the formation of a new carbon−carbon bond under mild conditions and provide two new rings: a carbocycle and a cyclic diazenium salt. The reactivity and synthetic utility of cyclic diazenium salts is currently under investigation and results from these studies will be reported in due course.

Experimental Section

I. Representative Experimental Procedure for the Preparation of 4-Chlorophenyl Hydrazones:[34]. 1-(4-Chlorophenyl)-2-(hept-6-en-2-ylidene)hydrazine (30e′). 4-Chlorophenyl hydrazine (0.636 g, 4.46 mmol, 1 equiv) was added to a mixture of hept-6-en-2-one (0.50 g, 4.46 mmol, 1 equiv) and 4-Å molecular sieves in CH_2Cl_2 (4 mL). After 1.5 h of stirring the sieves were removed by filtration and the solvent was removed in vacuo to provide 1-(4-chlorophenyl)-2-(hept-6-en-2-ylidene)hydrazine (**30e′**) in 89% yield as a 1:0.17 ratio of *E* and *Z* hydrazone diastereomers. The highly air-sensitive[35] product was typically of sufficient purity to use in subsequent

(34) (i) O'Connor, R. *J. Org. Chem.* **1961**, *26*, 4375. (ii) Yao, H. C.; Resnick, P. *J. Org. Chem.* **1965**, *30*, 2832. (iii) Harej, M.; Dolenc, D. *J. Org. Chem.* **2007**, *72*, 7214. (iv) Tiecco, M.; Testaferri, L.; Marini, C. S.; Bagnoli, L.; Temperini, A. *Tetrahedron* **1997**, *53*, 7311. (v) The hydrazones could also be prepared by mixing the ketone, 4-chlorophenyl hydrazine hydrochloride, and sodium acetate in ethanol under an atmosphere of nitrgen. The mixture was stirred at room temperature or heated to reflux (for sterically encumbered ketones) and the progress of the reaction was monitored by TLC. Upon completion, the solvent was removed in vacuo to provide the hydrazone, which could be further purified by dissolving the residue in pentane and passing the mixture through a short plug of basic alumina.

(35) Harej, M.; Dolenc, D. *J. Org. Chem.* **2007**, *72*, 7214.

reactions without further purification. Small quantities of α-azohydroperoxide could be removed by dissolving the impure hydrazone in pentane and passing the mixture through a short plug of basic alumina. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.84 (br s, 1H), 5.84 (ddt, J = 16.9, 10.4, 6.8 Hz, 1H), 5.03 (app dq, J = 17.3, 1.6 Hz, 1H), 4.96−4.99 (m, 1H), 2.31 (t, J = 7.5 Hz, 2H), 2.11 (q, J = 7.1 Hz, 2H), 1.85 (s, 3H), 1.68 (p, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 144.5, 138.4, 128.9, 123.9, 114.8, 114.0, 38.2, 33.3, 25.7, 14.4; MS (ESI) calcd for $[C_{13}H_{17}ClN_2H]^+$ 237.1158, found 237.1158. Observable resonances for the minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, J = 8.9 Hz, 2H), 5.06−5.11 (m, 2H), 2.24 (t, J = 8.3 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 144.4, 137.7, 115.8, 113.9, 28.4, 24.2, 23.1.

II. Characterization Data for 4-Chlorophenyl Hydrazones. (*E*)-1-(4-Chlorophenyl)-2-((*Z*)-oct-6-en-2-ylidene)hydrazine (30a′). Yield 83%; *E*/*Z* 1:0.1; major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.83 (br s, 1H), 5.41−5.44 (m, 1H), 5.33−5.44 (m, 1H), 2.32 (t, J = 7.6 Hz, 2H), 2.04−2.15 (m, 2H), 1.85 (s, 3H), 1.64 (p, J = 7.8 Hz, 2H), 1.60 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 144.6, 130.1, 129.0, 124.3, 123.9, 114.1, 38.4, 26.4, 14.4, 12.7; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, J = 8.8 Hz, 2H), 5.53−5.62 (m, 2H), 2.24 (app t, J = 7.5, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.4, 125.6, 123.9, 113.9, 28.6, 26.5, 24.9, 23.1, 12.9; MS (ESI) calcd for $[C_{14}H_{19}ClN_2H]^+$ 251.1315, found 251.1313.

(*E*)-1-(4-Chlorophenyl)-2-(7-methyloct-6-en-2-ylidene)hydrazine (30b′). Yield 94%; *E*/*Z* 1:0.3; major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 5.13 (tp, J = 7.2, 1.5 Hz, 1H), 2.30 (t, J = 7.7 Hz, 2H), 2.00−2.08 (m, 3H), 1.84 (s, 3H), 1.70 (s, 3H), 1.60 (s, 3H), 1.50−1.66 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 144.6, 131.9, 129.0, 124.2, 114.1, 38.5, 27.6, 26.7, 25.7, 17.7, 14.4; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, J = 8.7 Hz, 2H), 5.06−5.11 (m, 1H), 2.23 (t, J = 7.4 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.9, 113.9, 17.8; MS (ESI) calcd for $[C_{15}H_{21}ClN_2H]^+$ 265.1472, found 265.1475.

(2*E*,7*E*)-Methyl 7-(2-(4-chlorophenyl)hydrazono)oct-2-enoate (30c′). Yield 84%; major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.7 Hz, 2H), 6.99 (dt, J = 15.6, 7.1 Hz, 1H), 6.97 (d, J = 9.2 Hz, 2H), 6.87 (br s, 1H), 5.85 (dt, J = 15.6, 1.6 Hz, 1H), 3.73 (s, 3H), 2.33 (t, J = 7.5 Hz, 2H), 2.28 (qd, J = 7.5, 1.6 Hz, 2H), 1.84 (s, 3H), 1.77 (p, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 149.0, 146.2, 144.4, 128.9, 123.9, 121.3, 114.0, 77.3, 77.0, 76.8, 51.3, 38.0, 31.6, 24.6, 14.5; MS (ESI) calcd for $[C_{15}H_{19}ClN_2O_2H]^+$ 295.1213, found 295.1209.

(*Z*)-1-(4-Chlorophenyl)-2-(2-methyloct-7-en-3-ylidene)hydrazine (30f′). Yield 92%; *E*/*Z* 1:4.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 8.5 Hz, 2H), 6.99 (br s, 1H), 6.96 (d, J = 8.8 Hz, 2H), 5.80−5.95 (ddt, J = 16.6, 10.2, 6.6 Hz, 1H), 5.07−5.12 (m, 2H), 2.53 (sept, J = 6.9 Hz, 1H), 2.2−2.32 (m, 2H), 2.14 (q, J = 7.2 Hz, 2H), 1.62−1.65 (m, 2H), 1.14 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5 144.7, 137.7, 128.9, 123.7, 116.0, 113.9, 35.6, 33.7, 26.2, 24.4, 20.4; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.01−5.06 (m, 1H), 4.96−5.00 (m, 1H), 2.87 (sept, J = 6.8 Hz, 1H), 1.11 (d, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 138.8, 114.6, 33.5, 31.0, 26.9, 25.5, 18.8; MS (ESI) calcd for $[C_{15}H_{21}ClN_2H]^+$ 265.1472, found 265.1479.

(*E*)-1-(4-Chlorophenyl)-2-(4,4-dimethylhept-6-en-2-ylidene)hydrazine (30g′). Yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 9.2 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 6.87 (br s, 1H), 5.89 (ddt, J = 17.5, 10.2, 7.4 Hz, 1H), 5.00−5.08 (m, 2H), 2.22 (s, 2H), 2.05 (d, J = 7.5 Hz, 2H), 1.89 (s, 3H), 0.96 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 144.4, 135.4, 129.0, 123.9, 117.2, 114.0, 50.1, 46.8, 34.5, 27.3, 17.2; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, 8.6 Hz, 2H), 5.09−5.17 (m, 2H), 2.18 (s, 3H), 2.09 (d, 6.9 Hz, 2H), 1.03 (s, 6H); MS (ESI) calcd for $[C_{15}H_{21}ClN_2H]^+$ 265.1472, found 265.1470.

(*E*)-1-(Hept-6-en-2-ylidene)-2-(3-nitrophenyl)hydrazine (30h′). Yield 74%; *E*/*Z* 1:0.3; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.60−7.65 (m, 1H), 7.28−7.37 (m, 2H), 7.14 (br s, 1H), 5.84 (ddt, J = 16.9, 10.3, 6.9 Hz, 1H), 5.02−5.07 (m, 1H), 5.00 (br d, J = 10.1 Hz, 1H), 2.34 (t, J = 7.4 Hz, 2H), 2.13 (q, J = 7.0 Hz, 2H), 1.89 (s, 3H), 1.70 (p, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 148.9, 146.8, 138.3, 129.7, 118.5, 114.9, 113.9, 107.4, 38.2, 33.3, 25.7, 14.6; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (s, 1H), 2.27 (t, J = 7.7 Hz, 2H), 2.04 (s, 3H); MS (ESI) calcd for $[C_{13}H_{17}N_3O_2H]^+$ 248.1399, found 248.1402.

(*E*)-1-(Hept-6-en-2-ylidene)-2-(4-methoxyphenyl)hydrazine (30i′). Yield 92%; *E*/*Z* 1:0.2; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9, 2H), 6.69 (br s, 1H), 5.84 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 4.93−5.06 (m, 2H), 3.76 (s, 3H), 2.30 (t, J = 7.3 Hz, 2H), 2.08−2.16 (m, 2H), 1.84 (s, 3H), 1.68 (p, J = 7.6, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 146.4, 140.3, 138.6, 114.7, 114.7, 114.3, 77.3, 77.0, 76.8, 55.7, 38.3, 33.3, 25.9, 14.4; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05−5.11 (m, 2H), 2.24 (t, J = 8.0 Hz, 2H), 2.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.7, 114.2, 28.5, 24.2, 23.1; MS (ESI) calcd for $[C_{14}H_{20}N_2OH]^+$ 233.1654, found 233.1652.

(*E*)-1-(4-Chlorophenyl)-2-(oct-7-en-2-ylidene). Yield 87%; *E*/*Z* 1:0.2; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.83 (br s, 1H), 5.82 (ddt, J = 17.6,10.7, 6.9 Hz, 1H), 4.93−5.04 (m, 2H), 2.30 (t, J = 7.8 Hz, 2H), 2.06−2.13 (m, 2H), 1.84 (s, 3H), 1.56−1.62 (m, 2H), 1.41−1.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 144.6, 138.8, 129.0, 124.0, 114.5, 114.1, 38.7, 33.6, 28.5, 26.0, 14.4; observable resonances for minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (t, J = 7.7 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.5, 25.1; MS (ESI) calcd for $[C_{14}H_{19}ClN_2H]^+$ 251.1315, found 251.1317.

III. Representative Experimental Procedure for the Preparation of Aryl-α-chloroazoalkanes:[36] 1-(2-Chlorohept-6-en-2-yl)-2-(4-chlorophenyl)diazene (12e′). Oxalyl chloride (5.15 mmol, 0.44 mL, 1.2 equiv) was added in a dropwise manner to a stirred solution of DMSO (5.58 mmol, 0.40 mL, 1.3 equiv) in THF (30 mL) at −55 °C under a nitrogen atmosphere. The reaction was maintained at −55 °C until gas evolution ceased (∼20 min) at which point the reaction was cooled further to −78 °C. A mixture of Et_3N (6.43 mmol, 0.90 mL, 1.5 equiv) and hydrazone **30e′** (1.02 g, 4.29 mmol, 1 equiv) in THF (5 mL) was added in a dropwise manner via cannula. An immediate

(36) The aryl-α-chloroazoalkane products were moderately stable, but decomposed on standing. Attempts to send the sample for exact mass determination failed to provide useful data.

color change and a concomitant formation of a white precipitate were noted. The reaction mixture was maintained at −78 °C for 30 min and was then removed from the cold bath and warmed to room temperature at which point the solids were removed by filtration through a medium porosity sintered-glass funnel. The filtrate was concentrated by rotary evaporation and the residue was dissolved in pentane (∼20 mL) and decanted away from an insoluble red oil. The pentane was removed in vacuo to provide 1-(2-chlorohept-6-en-2-yl)-2-(4-chlorophenyl)diazene (**12e′**) in 80% yield. This material was used in the subsequent step without further purification. Residual DMSO could be removed by washing the pentane solution with water before concentrating, but this step was not routinely performed as it lowered product recovery and was not necessary for the subsequent transformation. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dm, J = 8.6, 1.9 Hz, 2H), 7.48 (dm, J = 8.6, 1.9 Hz, 2H), 5.78 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.01 (app dq, J = 17.0, 1.6 Hz, 1H), 4.95−4.98 (m, 1H), 2.28 (ddd, J = 14.0, 12.0, 4.7 Hz, 1H), 2.17 (ddd, J = 14.0, 12.0, 4.6 Hz, 1H), 2.09 (q, J = 7.3 Hz, 2H), 1.89 (s, 3H), 1.60−1.70 (m, 1H), 1.44−1.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 138.0, 137.3, 129.3, 124.2, 115.1, 96.5, 42.2, 33.4, 28.7, 23.4.

IV. Characterization Data for 4-Chlorophenyl-α-chloroazo Alkanes. (*E*)-1-((*Z*)-2-Chlorooct-6-en-2-yl)-2-(4-chlorophenyl)-diazene (12a′). Yield 83%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 5.44−5.50 (m, 1H), 5.32−5.38 (m, 1H), 2.28 (ddd, J = 14.1, 11.9, 4.7 Hz, 1H), 2.17 (ddd, J = 14.1, 11.9, 4.7 Hz, 1H), 2.08 (q, J = 7.3 Hz, 2H), 1.89 (s, 3H), 1.54−1.68 (m, 1H), 1.59 (d, J = 6.7 Hz, 3H), 1.41−1.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 137.3, 129.7, 129.3, 124.6, 124.2, 96.5, 42.3, 28.7, 26.5, 24.1, 12.8.

1-(2-Chloro-7-methyloct-6-en-2-yl)-2-(4-chlorophenyl)diazene (12b′). Yield 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 5.08 (t, J = 7.1 Hz, 1H), 2.25 (ddd, J = 14.0, 11.8, 4.5 Hz, 1H), 2.16 (ddd, J = 14.0, 11.8, 4.6 Hz, 1H), 2.01 (q, J = 7.3 Hz, 2H), 1.89 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.55−1.65 (m, 1H), 1.40−1.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 137.2, 132.0, 129.2, 124.2, 123.8, 96.5, 42.4, 28.6, 27.7, 25.6, 24.4, 17.7.

(*E*)-Methyl 7-Chloro-7-((*E*)-(4-chlorophenyl)diazenyl)oct-2-enoate (12c′). Yield 69%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 6.94 (dt, J = 15.7, 7.0, Hz, 1H), 5.83 (dt, J = 15.7, 1.5 Hz, 1H), 3.72 (s, 3H), 2.30 (ddd, J = 14.0, 11.8, 4.6 Hz, 1H), 2.25 (qd, J = 7.3, 1.4 Hz, 2H), 2.18 (ddd, J = 14.1, 12.9, 4.6 Hz), 1.89 (s, 3H),1.68−1.78 (m, 2H), 1.51−1.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 149.6, 148.6, 137.8, 129.7, 124.6, 121.9, 96.4, 51.8, 42.9, 42.5, 32.1, 31.7, 30.3, 29.1, 23.0, 22.2.

1-(3-Chloro-2-methyloct-7-en-3-yl)-2-(4-chlorophenyl)diazene (12f′). Yield 95%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 5.74 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.95 (app dq, J = 17.1, 1.7 Hz, 1H), 4.92−4.96 (m, 1H), 2.65 (septet, J = 6.71 Hz, 1H), 2.37 (ddd, J = 14.1, 11.8, 4.6 Hz, 1H), 2.20 (ddd, J = 14.0, 12.0, 4.4 Hz, 1H), 2.05 (q, J = 7.2 Hz, 2H), 1.55−1.64 (m, 1H), 1.21−1.30 (m, 1H), 1.15 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 138.0, 137.1, 129.3, 124.1, 115.0, 104.2, 39.3, 37.7, 33.5, 22.9, 17.5, 17.4.

1-(2-Chloro-4,4-dimethylhept-6-en-2-yl)-2-(4-chlorophenyl)-diazene (12g′). Yield 86%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 5.81 (ddt, J = 17.1, 9.79, 7.5 Hz, 1H), 4.96−5.07 (m, 2H), 2.50 (d, J = 15.5 Hz, 1H), 2.30 (d, J = 15.5 Hz, 1H), 1.96−2.1 (m, 2H), 1.91 (s, 3H), 0.95 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 137.4, 135.0, 129.4, 124.3, 117.6, 96.6, 53.7, 48.5, 34.8, 31.6, 28.5, 28.4.

1-(2-Chlorohept-6-en-2-yl)-2-(3-nitrophenyl)diazene (12h′). Yield 75%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.70 (t, J = 8.2 HZ, 1H), 5.80 (ddt, J = 17.0, 10.2, 6.9 Hz, 1H), 4.95−5.06 m (2H), 2.31 (ddd, J = 14.1, 11.8, 4.7 Hz, 1H), 2.21 (ddd, J = 14.4, 11.9, 4.6 Hz, 1H), 2.09 (q, J = 6.9 Hz, 2H), 1.93 (s, 3H), 1.59−1.71 (m, 1H), 1.44−1.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 148.9, 137.8, 130.1, 129.4, 125.4, 117.0, 115.2, 96.5, 42.0, 33.3, 28.7, 23.4.

1-(2-Chlorohept-6-en-2-yl)-2-(4-methoxyphenyl)diazene (12i′). Yield 82%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 5.78 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H), 5.01 (app d, J = 17.2 Hz, 1H), 4.93−4.98 (app d, J = 10.4 Hz, 1H), 3.87 (s, 3H), 2.27 (ddd, J = 14.2, 12.0, 4.7 Hz, 1H), 2.16 (ddd, J = 14.1, 11.9, 4.7 Hz, 1H), 2.09 (q, J = 7.0 Hz, 2H), 1.88 (s, 3H), 1.58−1.70 (m, 1H), 1.46−1.57 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 145.1, 138.2, 124.9, 115.0, 114.1, 96.5, 55.6, 42.4, 33.5, 28.8, 23.5.

(*E*)-1-(2-Chlorooct-7-en-2-yl)-2-(4-chlorophenyl)diazene (24). Yield 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 5.78 (ddt, J = 16.9, 10.1, 6.8 Hz, 1H), 4.90−5.04 (m, 2H), 2.24−2.32 (m, 1H), 2.13−2.20 (m, 1H), 2.01−2.10 (m, 2H), 1.89 (s, 3H), 1.51−1.59 (m, 1H), 1.37−1.46 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 138.8, 137.7, 129.7, 124.6, 115.0, 96.9, 43.0, 33.8, 29.1, 29.0, 24.0.

V. Representative Experimental Procedures for the Formation of Bicyclic Diazenium Salts. Method A: Lewis acid-mediated formation of bicyclic diazenium salts from α-chloroazo compounds:

6a-Methyl-2-(4-chlorophenyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13e′). Antimony pentachloride (3.56 mmol, 0.455 mL, 1 equiv) was added dropwise to a stirred solution of the α-chloroazoalkane **12e′** (3.56 mmol, 0.965 g, 1 equiv) in CH_2Cl_2 (40 mL) at −60 °C under a nitrogen atmosphere. The cooling bath was allowed to warm slowly to 0 °C (∼45 min) and the reaction was maintained at that temperature for 1 h. The mixture was allowed to stir at room temperature for 10 min at which point the solvent was removed in vacuo to provide a dark oil or foam. This crude material was analyzed by proton NMR (CD_3CN) to determine the ratio of fused to bridged diazenium salt products. The NMR sample was recombined with the crude reaction mixture, the solvent was removed in vacuo, and the residue was triturated with Et_2O to provide the desired diazenium salt as a powder in 92% yield: ^{1}H NMR (500 MHz, CD_3CN) δ 8.09 (d, J = 9.1 Hz, 2H), 7.76 (d, J = 9.3 Hz, 2H), 5.54 (dd, J = 17.2, 9.2 Hz, 1H), 5.13 (dd, J = 17.2, 4.5 Hz, 1H), 2.92−2.97 (m, 1H), 2.45−2.54 (m, 1H), 2.03−2.17 (m, 2H), 1.80 (s, 3H), 1.72−1.82 (m, 2H), 1.45−1.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 139.1, 131.7, 126.7, 101.2, 78.0, 43.2, 39.8, 33.7, 25.1, 23.8; observable resonances for minor isomer: 6-(4-chlorophenyl)-1-methyl-6,7-diazabicyclo[3.2.1]oct-6-en-6-ium hexachlorostibate(V) (**14e′**): ^{1}H NMR (500 MHz, CD_3CN) δ 8.09 (d, J = 6.6 Hz, 2H), 7.79 (d, J = 6.1 Hz, 2H), 6.05 (app t, J = 5.1 Hz, 1 H), 1.87 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 144.6, 132.3, 87.5, 83.7, 29.4, 22.9, 22.6, 18.4; IR (ATR, cm^{-1}) 1586, 1529, 1413, 1095, 831; MS (ESI) calcd for $[C_{13}H_{16}ClN_2]^+$ 235.1002, found 235.0998.

Method B: Dimethyl sulfide ditriflate mediated formation of bicyclic diazenium salts from hydrazones:

6a-Methyl-2-(4-chlorophenyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Triflate (31e′). Trifilic anhydride (0.82 mmol, 0.14 mL, 1.1 equiv) was added dropwise to a −78 °C solution of DMSO (0.86 mmol, 0.06 mL, 1.15 equiv) in CH_2Cl_2 (32 mL). After 20 min a solution of 4-chlorophenyl hydrazone (0.75 mmol, 0.18 g, 1 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (0.89 mmol, 0.18 g, 1.2 equiv) in CH_2Cl_2 (5 mL) was added. The resulting bright yellow solution was stirred for 20 min during which time a fine precipitate often formed. The dry ice dewar was removed and the solution was allowed to warm to room temperature over 30 min during which time the silky precipitate dissolved and an orange solution resulted. Upon warming to room temperature, a known quantity of dibenzyl ether (0.37 mmol, 0.07 mL, 0.5 equiv) was added to the reaction mixture as an internal NMR standard and the solvent was removed in vacuo at 60 Torr to provide an orange powder. The ratio of diazenium salt to dibenzyl ether was determined by proton NMR analysis (CD_3CN), which showed the desired product had formed in 67% yield. Spectroscopic data matched that of hexachlorostibate salts **13e′** and **14e′**.

VI. Characterization Data for the Diazenium Salt Products. 2-(4-Chlorophenyl)-3,6a-dimethyl-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13a′) or Triflate (31a′). Method A yield 87%; Method B yield 61%; ^{1}H NMR (500 mHz, CD_3CN) δ 7.95 (d, J = 9.1 Hz, 2H), 7.76 (d, J = 9.1 Hz, 2H), 5.94 (dq, J = 9.3, 7.2 Hz, 1H), 2.96−3.00 (m, 1H), 2.45−2.53 (m, 1H), 2.18−2.25 (m, 1H), 1.76−1.92 (m, 3H), 1.79 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H), 1.42−1.53 (m, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 142.8, 138.1, 131.5, 127.3, 99.8, 84.6, 46.9, 39.7, 28.6, 25.6, 24.1, 15.7; IR (ATR, cm^{-1}) 1518, 1441, 1409, 1095, 832; MS (ESI) calcd for $[C_{14}H_{18}ClN_2]^+$ 249.1158, found 249.1153.

2-(4-Chlorophenyl)-3-(methoxycarbonyl)-6a-methyl-1,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13c′) or Triflate (31c′). Method A yield 69%; Method B yield 44%; ^{1}H NMR (500 MHz, CD_3CN) δ 8.07 (s, 1H), 7.60−7.66 (m, 4H), 3.93 (dd, J = 9.8, 5.0 Hz, 1H), 3.79 (s, 3H), 2.27−2.37 (m, 2H), 2.09−2.18 (m, 1H), 1.76−1.88 (m, 3H), 1.57 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 157.2, 151.0, 139.7, 134.5, 130.78, 127.5, 73.8, 58.8, 55.0, 42.9, 34.2, 26.0, 25.9; IR (ATR, cm^{-1}) 1746, 1515, 1436, 1096, 838, 829; MS (ESI) calcd for $[C_{15}H_{18}O_2ClN_2]^+$ 293.1057, found 293.1056.

6a-Isopropyl-2-(4-chlorophenyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13f′) or Triflate (31f′). Method A yield 80%; Method B yield 66%; ^{1}H NMR (500 MHz, CD_3CN) δ 8.12 (d, J = 9.2 Hz, 2H), 7.76 (d, J = 9.2 Hz, 2H), 5.53 (dd, J = 17.5, 9.8 Hz, 1H), 5.14 (dd, J = 17.5, 4.4 Hz, 1H), 3.11−3.16 (m, 1H), 2.43 (septet, J = 6.5 Hz, 1H), 2.37−2.40 (m, 1H), 2.23−2.29 (m, 1H), 1.90−1.98 (m, 1H), 1.74−1.81 (m, 2H), 1.41−1.50 (m, 1H), 1.16 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 144.0, 139.0, 131.8 (t), 127.0 (m), 108.7, 78.0, 40.1, 37.2, 35.4, 33.8, 24.6, 18.6, 18.3; observable resonances for minor isomer: 6-(4-chlorophenyl)-1-isopropyl-6,7-diazabicyclo[3.2.1]oct-6-en-6-ium hexachlorostibate(V) (**14f′**) or triflate (**32f′**): ^{1}H NMR (500 MHz, CD_3CN) δ 8.19 (d, J = 9.3 Hz, 2H), 7.79 (d, J = 9.3 Hz, 2H), 6.04−6.10 (m, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 38.8, 34.5, 25.4, 22.9, 18.4, 17.9; IR (ATR, cm^{-1}) 1530, 1414, 1092, 828; MS (ESI) calcd for $[C_{15}H_{20}ClN_2]^+$ 263.1315, found 263.1319.

5,5,6a-Trimethyl-2-(4-chlorophenyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13g′) or Triflate (31g′). Method A yield 89%; Method B yield 54%; ^{1}H NMR (500 MHz, CD_3CN) δ 8.11 (d, J = 9.1 Hz, 2H), 7.76 (d, J = 9.3 Hz, 2H), 5.41 (dd, J = 16.2, 7.9 Hz, 1H), 5.23 (dd, J = 16.2, 2.3 Hz, 1H), 3.12 (qd, J = 8.0, 2.3 Hz, 1H), 2.26 (d, J = 13.9 Hz, 1H), 2.20 (dd, J = 14.3, 1.7 Hz, 1H), 2.05 (ddd, J = 13.1, 8.3, 1.6 Hz, 1H), 1.75 (s, 3H), 1.47 (ddd, J = 13.1, 9.3, 1.6 Hz, 1H), 1.13 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 143.9, 139.2, 131.8, 127.0, 101.0, 77.0, 51.2, 47.6, 43.2, 39.8, 28.5, 28.3, 25.0; observable resonances for minor isomer: 6-(4-chlorophenyl)-1,3,3-trimethyl-6,7-diazabicyclo[3.2.1]-oct-6-en-6-ium hexachlorostibate(V) (**14g′**) or triflate (**32g′**): ^{1}H NMR (500 MHz, CD_3CN) δ 8.18 (d, J = 9.1 Hz, 2H), 7.82 (d, J = 9.3 Hz, 2H), 5.94−5.96 (m, 1H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 132.7, 126.7, 87.6, 81.7, 43.0, 36.4, 31.7, 23.2; IR (ATR, cm^{-1}) 1524, 1412, 1094, 831; MS (ESI) calcd for $[C_{15}H_{20}ClN_2]^+$ 263.1315, found 263.1312.

6a-Methyl-2-(3-nitrophenyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13h′). Method A yield 81%; proton NMR resonances assignable to **13h′**: ^{1}H NMR (500 MHz, CD_3CN) δ 8.87 (t, J = 2.1 Hz, 1H), 8.68 (dd, J = 8.3, 1.7 Hz, 1H), 8.46 (dd, J = 8.3, 2.2 Hz, 1H), 8.01 (t, J = 8.3 Hz, 1H), 5.61 (dd, J = 17.3, 9.7 Hz, 1H), 5.23 (dd, J = 17.3, 4.2 Hz, 1H), 2.97−3.05 (m, 1H), 1.86 (s, 3H); proton NMR resonances assignable to 1-methyl-6-(3-nitrophenyl)-6,7-diazabicyclo[3.2.1]oct-6-en-6-ium hexachlorostibate-(V) (**14h′**): ^{1}H NMR (500 MHz, CD_3CN) δ 8.93 (t, J = 2.1 Hz, 1H), 8.71 (dd, J = 8.3, 1.7 Hz, 1H), 8.54 (dd, J = 8.3, 2.4 Hz, 1H), 8.04 (t, J = 8.4 Hz, 1H), 6.17 (t, J = 5.2 Hz, 1H), 2.38 (d, J = 11.8 Hz, 1H), 1.93 (s, 3H), 0.92−1.04 (m, 1H); proton NMR resonances assignable to **13h′** and **14h′**: 2.52−2.62 (m, 2H), 1.74−2.22 (m, 10 H); carbon NMR resonances assignable to **13h′** and **14h′**: ^{13}C NMR (125 MHz, CD_3CN) δ 150.1, 149.6, 140.6, 139.2, 133.3, 132.8, 131.8, 131.2, 130.5, 130.4, 120.2, 120.1, 101.7, 88.5, 84.5, 78.5, 43.1, 43.0, 39.7, 33.4, 29.1, 24.7, 23.6, 22.6, 22.0, 18.0; IR (ATR, cm^{-1}) 1529, 1454, 1349, 803, 735; MS (ESI) calcd for $[C_{13}H_{16}N_3O_2]^+$ 246.1243, found 246.1248.

6a-Methyl-2-(4-methoxyphenyl)-3,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazol-2-ium Hexachlorostibate(V) (13i′). Method A yield 92%; ^{1}H NMR (500 MHz, CD_3CN) δ 8.09 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.9 Hz, 2H), 5.47 (dd, J = 16.7, 9.7 Hz, 1H), 5.07 (dd, J = 16.7, 4.1 Hz, 1H), 3.97 (s, 3H), 2.86−2.93 (m, 1H), 2.41−2.47 (m, 1H), 2.03−2.08 (m, 2H), 1.76 (s, 3H), 1.98−2.03 (m, 1H), 1.41−1.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 132.2, 126.6 (br), 115.5, 98.1, 75.8, 56.1, 41.8, 38.4, 32.4, 23.7, 22.5; IR (ATR, cm^{-1}) 1580, 1513, 1429, 1246, 1171, 1097, 1021, 835; MS (ESI) calcd for $[C_{14}H_{19}N_2O]^+$ 231.1497, found 231.1498.

7-(4-Chlorophenyl)-1-methyl-7,8-diazabicyclo[4.2.1]non-7-en-7-ium Hexachlorostibate(V) (26). Method A yield 62%; ^{1}H NMR (500 MHz, CD_3CN) δ 8.14 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H), 6.08−6.10 (m, 1H), 2.67 (d, J = 13.3 Hz, 1H), 2.36−2.41 (m, 2H), 2.02−2.21 (m, 3H), 1.86 (s, 3H), 1.68−1.77 (m, 2H), 1.24−1.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 137.2, 132.2, 126.9 (br), 90.7,85.2, 41.2, 35.6, 33.5, 25.7, 24.6, 23.9; IR (ATR, cm^{-1}) 1519, 1411, 1094, 829; MS (ESI) calcd for $[C_{14}H_{18}ClN_2]^+$ 249.1158, found 249.1153.

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Supporting Information Available: General experimental details and copies of ^{1}H and ^{13}C NMR spectra for compounds **12a′**−**c′**, **12e′**−**i′**, **13a′**, **13c′**, **13e′**−**i′**, **14e′**−**h′**, **24**, **26**, **30a′**−**c′**, **30e′**−**i′**, **31a′**, **31c′**, **31e′**−**g′**, **32e′**−**g′**. This material is available free of charge via the Internet at http://pubs.acs.org.