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3,5,7-Trimethyl-1-azatricyclo[3.3.1.1^{3,7}]decan-2-ylidene, an Aminocarbene without π Conjugation

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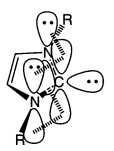
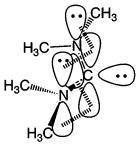
3,5,7-Trimethyl-1 -azatricyclo[3.3.1.1^{3,7}]decan-2-ylidene, an aminocarbene without π conjugation, has been generated from the corresponding tosylhydrazone salt. Addition of the carbene to alkenes is stereospecifically cis, thus showing that the reacting state is singlet. Competition studies reveal that the carbene is somewhat nucleophilic, implying a measure of overlap between the lone pair on nitrogen and the empty orbital on carbon. In turn, such overlap implies a pyramidal structure for the divalent carbon.

Aminocarbenes have a venerable history. Forty years ago, they were known to have unusual, sometimes remarkable properties. For example, carbenes substituted with a pair of nitrogen atoms are the archetypal nucleophilic divalent reagents,[1] and there were hints that diaminocarbenes were available by dissociation of their dimers, a quite spectacular phenomenon.[2] Despite these early landmarks, it is their appearance in modern times as *isolable* divalent species that will surely be their longest lasting legacy.[3] There is a clear connection between the historical record and the modern isolation. It was Wanzlick's goal to isolate a stable carbene, for instance, he was just too far ahead of his time in his thinking to be successful.

That singlet diaminocarbenes can be isolated depends critically on the ability of nitrogen to donate π electrons into the vacant 2p orbital of the singlet carbene, as shown for imidazol-2-ylidene **1**[3a] and Alder and Blake's spectacular bis(dimethylamino)carbene **2**.[4]



1, R = adamantyl



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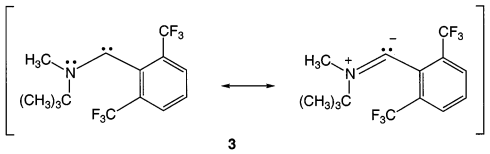
Most recently, it has been shown by the Bertrand group that a single amino nitrogen, coupled with some steric stabilization of the divalent carbon, is sufficient for room temperature stability of the carbene **3**.[5] As in carbenes **1** and **2**, the nitrogen again functions to donate its lone pair electrons to the empty 2p orbital of the carbene.[5] Other



3

atoms such as oxygen and the halogens that can donate π electrons into the vacant carbene p prbital also produce ground-state singlets that sometimes show nucleophilic behavior.[6] In these cases stabilization is just not great enough to result in isolable singlets. The question we set out to answer was what would be the properties of an aminocarbene without the critical π donation so evident in **3**, for example? In this paper we begin the answer, showing that a monoaminocarbene without dominant π donation reacts as a singlet state. The question of the ground state is more complex and we will soon report a computational study of this matter.[7] A competition experiment reveals evidence that our aminocarbene is still nucleophilic.

We began with "the most twisted amide", **4**,[8] itself available from Kemp's triacid.[9] As noted by Kirby,[8] compound **4** is only a nominal amide, and undergoes reactions characteristic of a normal ketone, such as

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(1) Wanzlick, H.-W. *Angew. Chem.* **1962**, *74*, 128.
(2) Lemal, D. M.; Lovald, R. A.; Kawano, K. I. *J. Am. Chem. Soc.* **1964**, *86*, 2518.
(3) (a) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, *361*. (b) For a review of the Arduengo Group's work, see: Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913. (c) For a review of all stable carbenes, see: Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Alder, R. W. *Carbene Chemistry*; Bertrand, G., Ed.; Marcel Dekker: New York, 2002; Chapter 5.
(4) Alder, R. W.; Blake, M. E. *J. Chem. Soc., Chem. Commun.* **1997**, 1513.
(5) Sole, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901.
(6) Du, X. M.; Fan, H.; Goodman, J. L.; Kesselmayer, M. A.; Krough-Jespersen, K.; La Villa, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920.
(7) Ye, Q.; Bartlett K. L.; Nooijen, M.; Jones, M., Jr. In preparation.
(8) Kirby, A. J.; Komarov, I. V.; Wothers, P. D.; Feeder, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 785. Kirby, A. J.; Komarov, I. V.; Feeder, N. *J. Chem. Soc., Perkin Trans. 2* **2001**, 522.
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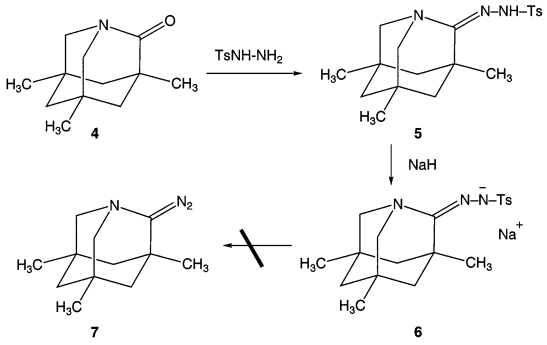
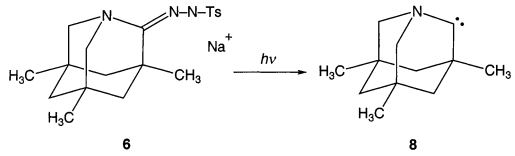
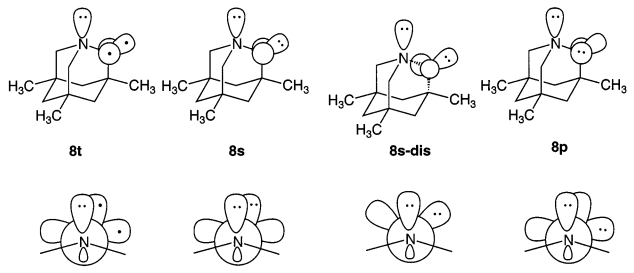
formation of an acetal and the Wittig reaction. This reactivity suggested that imine formation would be possible, and so it was. For example, we were able to make tosylhydrazone **5** from **4** and convert it into its sodium salt **6** with sodium hydride. Here, however, our



luck ran out, and we were unable to transform salt **6** into the corresponding diazo compound **7**. We had hoped that carbene **8**, which would have exactly the properties we sought, would be available from decomposition of the diazo compound **7**. As we could not make **7**, we took advantage of a known,[10] but very little used method of carbene generation, photolysis of the tosylhydrazone salt itself in heterogeneous medium.

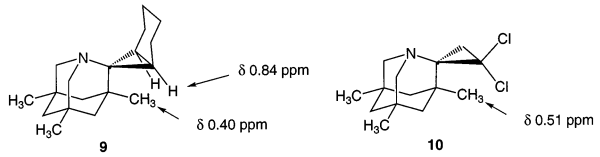


It is worthwhile to pause and consider the possible structures for this carbene. There is the usual choice of singlet and triplet, but the presence of a lone pair formally orthogonal to the 2p orbital introduces some interesting possibilities for the singlet. Triplet **8** will have a single electron in each of the two orbitals, and presumably, the stabilization afforded by the filled−half-filled interaction will favor the symmetrical structure **8t**. Ordinarily, singlet carbenes have a structure such as **8s**, in which the paired nonbonding electrons occupy the lower energy hybrid orbital. The p^2 singlet (**8p**) or a singlet in which both the p and hybrid orbital are singly occupied are substantially higher energy species. In this carbene, the symmetrical version of the singlet, **8s**, is destabilized by the filled−filled orbital interaction required by the geometry. One would surely expect that singlet **8** would distort to gain filled−empty overlap and to minimize the destabilizing filled−filled interaction as in **8s-dis**. Bridgehead alkenes such as adamantene rehybridize for similar reasons.[11] If the structure **8s-dis** contributes significantly, one would anticipate that carbene **8** would show nucleophilic behavior.



Before dealing with the subtle questions, we had to know whether photolysis of the tosylhydrazone salt would yield carbene **8**, and whether **8** would even add to alkenes. A 450-W Hanovia medium-pressure mercury arc was used to irradiate sealed Pyrex tubes containing about 10 mL of substrate and 30 mg of apparently undissolved salt under argon. After 4 h of irradiation, the tubes were cooled and opened, and the liquids were separated from residual solids. Analysis was by gas chromatography followed by product separation and spectroscopy. The full details can be found in the Experimental Section.

Irradiation of salt **6** in cyclohexene led to a single adduct, **9**.[12] Compound **9** showed no signals in the ^{1}H NMR spectrum in the region associated with hydrogens attached to double bonds. It was likely that **9** was the cyclopropane adduct. Confirmation comes from the observation of a pair of equivalent hydrogens at 0.84 ppm, and a 3H signal at 0.40 ppm. The high-field peak is appropriate for a hydrogen poised beneath the face of a three-membered ring,[13] but for little else. At this point we cannot prove that the stereochemistry is as assigned in **9**, with the ring anti to the bridgehead methyl group. The stereochemistry will be assigned in a moment by analogy to the 2-butene adducts, for which we have NOE data that make the determination possible.



Addition also takes place to 1,1-dichloroethylene to give compound **10**, which also lacks hydrogens attached to a double bond, and has a single high-field methyl signal at 0.51 ppm.

Given that addition of this potentially unusual carbene takes place, and that our somewhat unorthodox photolysis procedure yields cyclopropanes in usable amounts, we can move on to the question of the stereochemistry of the cyclopropanation reaction. Irradiation of **6** in *trans*-2-butene led to a single adduct **11** in 34% isolated yield.[14] Compound **11** showed two cyclopropane methyl signals in its ^{1}H NMR spectrum at 1.15 and 1.33 ppm. The observation of two new methyl groups excludes either cis diastereomer as a possible structure. Once again, there was a single high-field signal for the methyl group underneath the three-membered ring at 0.61 ppm.

(10) Kirmse, W.; Pook, K. H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 594.

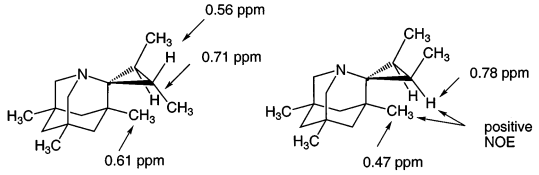
(11) Michl, J.; Radziszewski, J. G.; Downing, J. W.; Kopecky, J.; Kazynski, P.; Miller, R. *D. Pure Appl. Chem.* **1987**, *59*, 1613. Bian, N.; Jones, M., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 8957.

(12) All new compounds showed appropriate high-resolution mass spectra. See the Experimental Section for details.

(13) Jackman, L. M.; Sternhell *Applications of NMR Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969; pp 98−101.

(14) This reaction was quantified to show that we were not dealing with trace products. The yield is based on starting tosylhydrazone and thus represents the overall yield of a series of four reactions: salt formation, diazo compound formation, carbene generation, and cycloaddition. Losses in isolation undoubtedly also occurred. The other cycloaddition reactions were not quantified, were compared to this one, and were not significantly different.

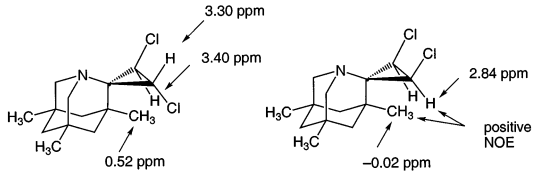
Irradiation in *cis*-2-butene led to a different cyclopropane, **12**, in which a 3H high-field methyl signal at 0.47 ppm was accompanied by a single 6H ring-methyl signal at 1.11 ppm. Thus, only one of the two possible cis cyclopropane adducts is formed. One's intuitive feeling that the methyl groups on the cyclopropane ring must be directed away from the single methyl group below the ring is confirmed by NOE experiments. For example, a positive NOE is observed in the cyclopropane hydrogens when the high-field methyl hydrogens at 0.47 ppm are irradiated.



11 **12**

The chemical shifts of the various cyclopropyl hydrogens can be used to add weight to the surmise that the cyclohexene adduct **9** has the stereochemistry shown. The chemical shift of the cyclopropyl hydrogens in **9**, 0.84 ppm, is more consistent with the shifts of 0.71 ppm (**11** syn) and 0.78 ppm (**12** syn) than with 0.56 ppm (**11** anti).

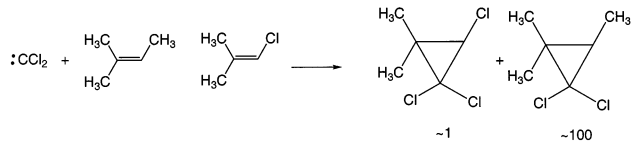
Similar results are obtained with *cis*- and *trans*-1,2-dichloroethylene. The trans alkene gives **13**, a cyclopropane containing two different cyclopropyl hydrogens, whereas the cis alkene gives a different cyclopropane **14** that NOE analysis shows to have the stereochemistry shown. There is no intercontamination of stereoisomers in the two reactions.



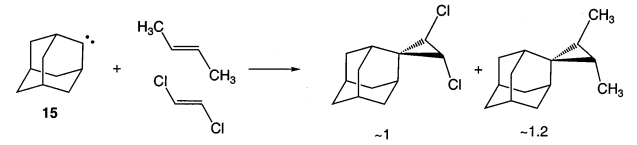
13 **14**

Stereochemistry is retained in both addition reactions. This result is the hallmark of singlet reactivity,[15] and it can be concluded with confidence that **8** is reacting in a singlet state, not the triplet. Of course, these experiments do not speak to the question of the ground state. Many ground-state triplets form products through their higher energy, more reactive singlet states. The archetypal methylene is a perfect example. The triplet lies about 9 kcal/mol below the singlet, but essentially all reactivity of methylene issues from the singlet state.[16] To determine the ground state of **8**, we must rely primarily on theory,[7] but we can note here that all attempts to detect a triplet EPR signal have come to naught.[17] The absence of an EPR signal indicates that the singlet state may indeed fall below the triplet state.

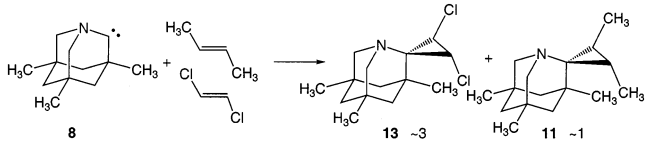
We already know experimentally that singlet reactivity is observed. Data from competition experiments show that carbene **8** is somewhat more nucleophilic than similar carbenes not containing nitrogen, presumably through the distortion that creates interaction between the lone pair on nitrogen and the empty orbital on the carbene. There are few reported competition experiments between alkenes and chloroalkenes, but what little data there are confirm the idea that an alkene substituted with an electron-withdrawing chlorine should be a poor competitor for a normal electrophilic carbene. For example, 2-methyl-2-butene is about 100 times more reactive toward dichlorocarbene than 1-chloro-2-methylpropene.[18] A few other examples, all consistent, can be gleaned from Moss' review.[19] Data on competitions



involving nucleophilic carbenes are even more sparse.[19] One nucleophilic singlet, methoxymethylcarbene, adds to 1-chloro-1-cyanoethene (note the complicating presence of the π accepting cyano group) 22 300 times faster than to 2-methyl-2-butene.[20] One might worry about steric effects induced by the cage structure of carbene **8**, so we compared **8** to **15**, a related and well-studied all-carbon cage,[21] using *trans*-1,2-dichloroethylene and *trans*-2-butene as competitors. As expected, carbene **15** "preferred" the unchlorinated alkene by a factor of about 1.2.



By contrast, carbene **8** gave cyclopropanes **13** and **11** in the ratio 3:1; the chlorocarbon is preferred in this case. Carbene **8** is more nucleophilic than is carbene **15**.



Similar results can be gathered from an examination of a competition using the cis alkenes, although the results are complicated by the presence of a third product, formed in about 17% yield in the reaction of **8** with *cis*-1,2-dichloroethylene. Carbene **15** reacts faster with the unchlorinated alkene by a factor of 3, whereas carbene

(15) Regitz, M., Ed. *Carbene(oide)*; Georg Thieme: Stuttgart, 1989. Kirmse, W. *Carbene Chemistry*; Academic: New York, 1971. Jones, M., Jr.; Moss, R. A. *Carbenes*; Wiley: New York, 1973; Vol. 1. Moss, R. A.; Jones, M., Jr. *Carbenes*; Wiley: New York, 1975; Vol. 2.

(16) See: Gaspar, P. P.; Hammond, G. S. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2, Chapter 6.

(17) We thank Professor Paul M. Lahti for valient attempts to find an ESR spectrum.

(18) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 6035, 7131.

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(20) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecek-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563.

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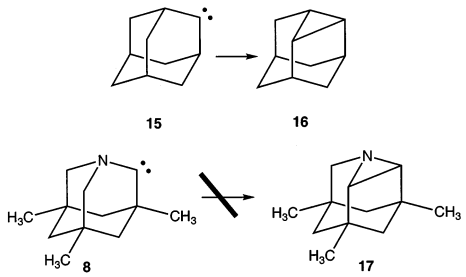
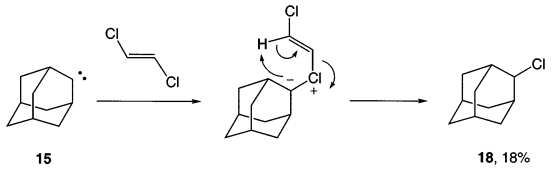
8 gives roughtly equal amounts of cis cyclopropanes. Once again, **8** is more nucleophilic than **15**.

Two other differences in the properties of **8** and **15** are consistent with the idea that **8** is not an ordinary electrophilic carbene. All additions of **15** are accompanied by substantial amounts of the product of intramolecular insertion, **16**. Like all carbon−hydrogen insertions, formation of **16** is initiated by interaction between the carbene LUMO, the empty 2p orbital, and the filled C−H σ bond. For example, the cyclopropane products from **15** in the competition experiment shown above are accompanied by 18% of **16**. We see no trace of the analogous product **17** that would be formed from **8**, as judged by the absense of an appropriate peak in the GC/MS. Of course, negative evidence is only negative evidence, and differs sharply from a positive observation in the weight that it can be given. Nonetheless, the absence of **17** is consistent with the absence of an empty 2p orbital to initiate the putative intramolecular insertion reaction in **8**.



Similarly, when **15** is generated in *trans*-1,2-dichloroethylene, 15−20% of 2-chloroadamantane (**18**) appears as a significant side product. We suggest that **18** is the result of initial ylide formation, followed by rearrangement. In support of this suggestion is the observation that only 2% of **18** appears when *cis*-1,2-dichloro-ethylene is used.



No monochloride is formed when **8** reacts in *cis*- or *trans*-1,2-dichloroethylene. Perhaps the increased nucleophilicity of **8** makes ylide formation unfavorable. Once again we have only negative evidence, but, once again, it is consistent with what we have come to expect of **8**.

Experimnental Section

General. All reagents were purchased from Aldrich Chemical Co. in >99% purity and checked by proton NMR spectroscopy before use. Further purification of specific reagents is described in the experimental procedure. Anhydrous solvents were obtained by distillation from various drying agents under argon.

Cyclohexane-1,3,5-tricarboxylic Acid. A mixture of 18 g (85 mmol) of trimesic acid, 2 g (10% mass equiv) of 5% rhodium on alumina,[22] and 300 mL of water was hydrogenated at 70 °C and 50 psi. Uptake was complete in 7 h and the yield was almost quantitative. The filtrate was concentrated to give a white solid. The acid obtained was mostly the cis,cis form (cis,cis/cis,trans = 7:1). Recrystalization from ethanol−toluene solution gave the cis,cis isomer, mp 218−219 °C (lit.[23] mp 218 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.51 (br s, 3H), 1.91 (dd, J = 5.5 Hz, J = 5.0 Hz, 3H), 1.83 (dd, J = 13.0 Hz, J = 5.0 Hz, 3H), 1.02 (dd, J = 13.0 Hz, J = 5.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 175.44, 40.79, 29.91; IR (cm^{-1}) 2917, 2850, 1708, 1616, 1418, 1289, 1261.

Trimethyl Cyclohexane-1,3,5-tricarboxylate. Method A.[24] Anhydrous methanol was distilled over CaH_2 before use. The cyclohexane-1,3,5-tricarboxylic acid (0.864 g, 2 mmol) was heated under reflux for 6 h with boron trifluoride−methanol complex (50% BF_3, 0.012 mol, 2.4 mL) in an excess of dry methanol (12 mL). The reaction mixture was cooled and poured into saturated sodium bicarbonate solution. It was then extracted with ether and dried over Na_2SO_4. After removal of ether, it afforded the trimethyl ester (0.82 g, 78%).

Method B. The cyclohexane-1,3,5-tricarboxylic acid (1.08 g, 0.005 mol) in 25 mL of anhydrous methanol was added dropwise to thionyl chloride (1.67 mL) in methanol solution. The mixture was heated to reflux under argon overnight. The thionyl chloride was carefully removed. This procedure gave the crude cyclohexane-1,3,5-tricarboxylic acid, trimethyl ester. Vacuum distillation gave a 92% yield, mp 48−49 °C (lit.[25] mp 48 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65 (s, 9H), 2.36 (dd, J = 5.5 Hz, J = 5.0 Hz, 3H), 2.25 (dd, J = 1.0 Hz, J = 5.0 Hz, 3H), 1.50 (dd, J = 13.0 Hz, J = 5.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 174.63, 52.03, 41.84, 30.56.

Trimethyl *cis,cis*-1,3,5-Trimethylcyclohexane-1,3,5-tricarboxylate.[26] Diisopropylamine was distilled from molecular sieves before use. LDA was generated at 0 °C by the addition of 2.5 M BuLi in hexanes (5.11 mL, 3.3 equiv) to diisopropylamine (1.8 mL, 3.3 equiv) in 10 mL of dry ether. To the remaining mixture was added dropwise 1 g of the trimethyl cyclohexane-1,3,5-tricarboxylate in 10 mL of ether. The mixture was stirred at 0 °C for 2 h. Then, 2 mL of dimethyl sulfate was added, and stirring was continued overnight at room temperature. The solution was washed with water, 1 N HCl, and brine, and then dried over Na_2SO_4. After solvent removal, 0.71 g of oil was obtained. GC-mass analysis showed that the ratio of the two isomers was cis,cis/cis,trans = 8:1. Fractional recrystalization from pentane−ether afforded pure cis,cis isomer as a white solid (40% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.51 (s, 9H), 2.54 (d, 3H), 1.14 (s, 9H), 1.09 (d, 3H); ^{13}C NMR (500 MHz, DMSO-d_6) δ 176.66, 51.96, 43.05, 41.49, 31.34.

***cis,cis*-1,3,5-Trimethylcyclohexane-1,3,5-tricarboxylic Acid**[27] **(Kemp's Triacid).** Trimethyl *cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylate (12 g, 0.04 mol) was dissolved in a mixture of 100 mL of methanol and 120 mL of 3 N NaOH. The solution was heated to 65 °C and stirred for 12 h. The methanol was removed by evaporation, the solution was cooled in an ice-bath, and the pH was adjusted to 1 with concentrated HCl. The triacid appeared as a white precipitate and was collected by suction filtration. The water layer was concentrated and chilled again to get more Kemp's triacid. The combined yield was 92% after no more crystals could be collected.

To the remaining mixture of cis,cis- and cis,trans-triacid was added a suitable amount of ether and the resulting solution was stirred vigorously for half an hour. The solution was filtered to get Kemp's triacid. This method was repeated several times, until no more pure Kemp's triacid could be collected: ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.01 (br s, 3H),

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3.34 (s, 9H), 1.2 (s, 6H); ^{13}C NMR (500 MHz, DMSO-d_6) δ 179.49, 41.18, 40.54, 30.46.

The synthesis of the twisted amide **4** from Kemp's triacid can be found in ref 8. Some workups were slightly different in our work but the synthetic route was basically the same as Kirby's.[8]

3,5,7-Trimethyl-1-azabicyclo[3.3.1.1^{3,7}]decane-2-tosylhydrazone (Twisted Amide Tosylhydrazone). THF was dried over sodium before use. Glassware was dried in the oven overnight and cooled in the desiccator over P_2O_5. Mg_2SO_4 was left in the desiccator for 3 days. To the stirring solution of the twisted amide (0.483 g, 2.5 mmol) in 50 mL of dry THF was added *p*-toluenesulfonylhydrazide (97%, 0.512 g, 2.75 mmol) in one portion. After mixing, excess dried Mg_2SO_4 was added. The solution was heated to gentle reflux. The reaction was monitored with ^{1}H NMR spectroscopy or TLC. The solvent was removed by evaporation and the crude product was purified by column chromatography to give a 60% yield of the twisted amide tosylhydrazone. Silica gel was used either freshly opened or predried in an oven (200 °C) overnight. The resulting twisted amide tosylhydrazone was easily hydrolyzed to give the twisted amide. Therefore, the sample should be stored under argon immediately after purification: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (br s, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 2.57 (d, J = 12.1 Hz, J = 2.5 Hz, 2H), 2.41 (s, 3H), 2.15 (d, J = 12.1 Hz, J = 2.5 Hz, 2H), 1.38 (d, J = 12.0 Hz, 1H), 1.32 (m, J = 12.0 Hz, J = 2.5 Hz, 5H), 1.08 (s, 3H), 0.67 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 164.32, 143.68, 135.77, 129.44, 128.02, 64.12, 51.60, 48.7, 37.34, 30.52, 25.8, 23.90, 21.73; IR (cm^{-1}) 3170, 2947, 2923, 2865, 1724, 1629, 1455, 1366, 1302, 1171, 1089; HRMS (EI) calcd for $C_{18}H_{27}N_3O_2S$ 361.18240, found 361.18197.

3,5,7-Trimethyl-1-azabicyclo[3.3.1.1^{3,7}]decane-2-tosylhydrazone Salt. Glassware was oven-dried and THF was distilled before use. Freshly opened NaH (powder, 95%, 1.2 equiv) was weighed into a round-bottomed flask capped with a septum. The twisted amide tosylhydrazone was dissolved in a minimum amount of dry THF and transferred to the round-bottomed flask with a syringe. After deprotonation was complete, THF was removed by a gentle argon flow and the resulting tosylhydrazone salt was available for use in the following photolysis.

General Procedure for the Photolysis. The photolyses were carried out in Pyrex tubes unless otherwise specified. The photolysis tube was dried in the oven, evacuated, and flushed with argon before use. Tosylhydrazone salt (30 mg) was transferred into a photolysis tube. The tube was degassed under vacuum and refilled with argon before addition of trapping solvents. The photolysis sample was degassed (freeze and thaw cycle) three times to remove residual moisture and air. The mixture in the photolysis tube was irradiated by a 450-W medium-pressure Hanovia lamp for 4 h at either room or ice temperature.

Photolysis of the Twisted Amide Tosylhydrazone Salt in Cyclohexene. Cyclohexene was distilled from $AlCl_3$ and stored in a Schlenk tube in the freezer before use. Cyclohexene (7−8 mL) was added to the photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was irradiated for 4 h at room temperature. At end of the first hour, the solution turned pink. When the irradiation was stopped, the solution was transferred to a vial and the photolysis tube was washed twice with ether. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (MeOH/CH_2Cl_2 = 0.3/2, R_f 0.73): ^{1}H NMR (500 MHz, C_6D_6) δ 2.6 (d, J = 12.0 Hz, 2H), 2.4 (d, J = 12.0 Hz, 2H), 1.78 (m, 3H), 1.65 (m, 5H), 1.3 (d, J = 12.0 Hz, 2H), 1.1 (dd, J = 12.0 Hz, 4H), 0.96 (d, J = 12.0 Hz, 2H), 0.84 (m, 2H), 0.68 (s, 6H), 0.39 (s, 3H); ^{13}C NMR (500 MHz, C_6D_6) δ 63.12, 50.60, 50.44, 50.22, 32.48, 30.29, 27.63, 24.54, 22.92,19.35,15.87; HRMS (EI) calcd for $C_{18}H_{29}N$ 259.23000, found 259.23130.

Photolysis of the Twisted Amide Tosylhydrazone Salt in *cis*-2-Butene. *cis*-2-Butene (10 mL) was condensed into a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was irradiated for 4 h at ice temperature. Then it was slowly brought to room temperature and the *cis*-2-butene was gently removed. The photolysis tube was washed twice with ether. The organic layers were combined, concentrated by evaporation, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (MeOH/CH_2Cl_2 = 0.3/2, R_f 0.53). The absolute yield was 6.8 mg (34%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (m, 4H), 1.38 (d, J = 11.5 Hz, 2H), 1.27 (d, J = 11.5 Hz,1 H), 1.24 (d, J = 11.5 Hz, 1H), 1.13 (d, J = 11.5 Hz, 2H), 0.98 (m, J = 11.3 Hz, J = 2.0 Hz, 6H), 0.84 (m, 2H), 0.75 (s), 0.47 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 2.52 (dd, J = 12.0 Hz, J = 2.0 Hz, 2H), 2.46 (dd, J = 12.0 Hz, J = 2.0 Hz, 2H), 1.28 (d, J = 12.0 Hz, 2H), 1.11 (m, 6H), 1.07 (dt, J = 12.0 Hz, J = 2.0 Hz, 2H), 0.96 (d, J = 12.0 Hz, 2H), 0.78 (m, 2H), 0.67 (s, 6H), 0.38 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 62.79, 50.55, 50.15, 49.93, 32.40, 30.13, 27.36, 24.03, 15.39, 6.89; HRMS (EI) calcd for $C_{16}H_{27}N$ 233.21435, found 233.21646.

Photolysis of the Twisted Amide Tosylhydrazone Salt in *trans*-2-Butene. *trans*-2-Butene (10 mL) was condensed into a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was irradiated for 4 h at ice temperature. Then it was slowly warmed to room temperature and the *trans*-2-butene was gently removed. The photolysis tube was washed twice with ether. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (MeOH/CH_2Cl_2 = 0.3/2, R_f 0.50): ^{1}H NMR (500 MHz, C_6D_6) δ 2.76 (dt, J = 12.5 Hz, J = 2.0 Hz, 1H), 2.53 (dt, J = 12.5 Hz, J = 2.0 Hz, 1H), 2.46 (dd, J = 12.5 Hz, J = 3.0 Hz, 1H), 2.44 (dd, J = 12.5 Hz, J = 3.0 Hz, 1H), 1.45 (dt, J = 12.0 Hz, J = 2.0 Hz, 1H), 1.36 (dt, J = 12.0 Hz, J = 2.*0* Hz, 1H), 1.33 (d, J = 7.*0* Hz, 3H,), 1.15 (d, J = 7.*0* Hz, 3H), 1.11 (dt, J = 12.0 Hz, J = 3.0 Hz, 1H), 1.06 (dt, J = 1.0 Hz, J = 3.0 Hz, 1H), 1.03 (dd, J = 12.0 Hz, J = 3.0 Hz, 1H), 0.90 (dd, J = 12.0 Hz, J = 3.0 Hz, 1H), 0.71 (qdd, J = 7.0 Hz, J = 7.0 Hz, J = 3.0 Hz, 1H), 0.69 (s, 3H), 0.66 (s, 3H), 0.63 (s, 3H), 0.56 (qdd, J = 7.0 Hz, J = 7.0 Hz, J = 3.0 Hz, 1H); ^{13}C NMR (500 MHz, C_6D_6) δ 63.81, 63.04, 53.24, 53.07, 50.67, 50.28, 33.34, 30.84, 29.74, 28.98, 27.6, 27.49, 26.44, 23.56, 15.47, 13.06; HRMS (EI) calcd for $C_{16}H_{27}N$ 233.21435, found 233.21463.

Photolysis of the Twisted Amide Tosylhydrazone Salt in *cis*-1,2-Dichloroethylene. *cis*-1,2-Dichloroethylene (10 mL) was added to a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was irradiated for 4 h at room temperature. Then the solution was transferred to a vial and the photolysis tube was washed twice with ether. The combined organic solutions were concentrated and analyzed by GC-mass spectrometry. The cyclopropane adduct was purified by preparative TLC (ether/pentane = 3/1, R_f 0.9): ^{1}H NMR (500 MHz, C_6D_6) δ 2.85 (s, 2H), 2.83 (dd, J = 12.0 Hz, J = 2.0 Hz, 2H), 2.42 (dd, J = 12.0 Hz, J = 2.0 Hz, 2H), 1.0 (d, J = 12.0 Hz, 2H), 0.94 (dt, J = 12.0 Hz, J = 2.0 Hz, 1H), 0.84 (dt, J = 12.0 Hz, J = 2.0 Hz, 1H), 0.72 (d, J = 1.0 Hz, 2H), 0.54 (s, 6H), −0.016 (s, 3H); ^{13}C NMR (500 MHz, C_6D_6) δ 61.96, 51.1, 49.27, 49.24, 38.53, 32.28, 29.96, 26.95, 23.74; HRMS (EI) calcd for $C_{14}H_{21}NCl$ 273.10510, found 273.10543.

Photolysis of the Twisted Amide Tosylhydrazone Salt in *trans*-1,2-Dichloroethylene. *trans*-1,2-Dichloroethylene (10 mL) was added to a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was irradiated for 4 h at room temperature. Then, the solution was transferred to a vial and the photolysis tube was washed twice with ether. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC

(ether/pentane = 0.3/2, R_f 0.7): ^{1}H NMR (500 MHz, C_6D_6) δ 3.40 (d, J = 4.0 Hz,1 H), 3.30 (d, J = 4.0 Hz,1 H), 2.80 (d, J = 12.5 Hz,1 H), 2.56 (d, J = 12.5 Hz, 1H), 2.34 (dt, J = 12.5 Hz, J = 3.0 Hz, 2H), 1.56 (d, J = 12.0 Hz, 1H), 1.16 (d, J = 12.0 Hz, 1H), 0.94 (dt, J = 12.5 Hz, J = 2.0 Hz, 1H), 0.89 (dt, J = 12.5 Hz, J = 2.0 Hz, 1H), 0.86 (dd, J = 1.0 Hz, J = 3.0 Hz, 1H), 0.76 (dd, J = 12.0 Hz, J = 3.0 Hz, 1H), 0.75 (s, 3H), 0.54 (s, 3H), 0.52 (s, 3H); ^{13}C NMR (500 MHz, C_6D_6) δ 63.59, 61.76, 56.02, 51.96, 49.4, 49.1, 48.17, 43.63, 32.99, 30.58, 29.32, 26.86, 26.80, 25.02; HRMS (EI) calcd for $C_{14}H_{21}NCl$ 273.10510, found 273.10426.

Photolysis of the Twisted Amide Tosylhydrazone Salt in 1,1-Dichloroethylene. 1,1-Dichloroethylene (10 mL) was added to a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was irradiated for 4 h at room temperature. Then, the solution was transferred to a vial, and the photolysis tube was washed with ether. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (ether/pentane = 1/1, R_f 0.73): ^{1}H NMR (500 MHz, C_6D_6) δ 2.99 (d, J = 12.0 Hz,1 H), 2.42 (d, J = 12.0 Hz, J = 2.0 Hz, 1H), 2.37 (d, J = 12.0 Hz, J = 2.0 Hz, 1H), 2.32 (d, J = 12.0 Hz, 1H), 1.66 (d, J = 12.0 Hz, 1H), 1.29 (d, J = 13.7 Hz 1H), 1.08 (d, J = 13.7 Hz, 1H), 1.06 (d, J = 12.0 Hz, 1H), 0.96 (d, J = 12.0 Hz, J = 2.0 Hz, 2H), 0.92 (d, J = 12.0 Hz, J = 2.0 Hz, 1H), 0.77 (s, 3H), 0.72 (dd, J = 12.0 Hz, J = 2.0 Hz, 1H), 0.58 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (500 MHz, C_6D_6) δ 66.26, 63.87, 63.04, 62.15, 52.48, 49.42, 48.85, 29.06, 27.29, 26.8, 26.5, 15.93; HRMS (EI) calcd for $C_{14}H_{21}NCl$ 273.10510, found 273.10508.

Photolysis of the Twisted Amide Tosylhydrazone Salt in a *cis*-2-Butene and *cis*-1,2-Dichloroethylene Mixture. *cis*-1,2-Dichloroethylene (2.8 mL, 0.037 mol) was added to a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was cooled with liquid nitrogen and degassed under vacuum. Then *cis*-2-butene (1.8 g, 0.032 mol) was transferred into the photolysis tube by condensation at liquid nitrogen temperature. The sample was degassed three times and irradiated for 4 h at room temperature. The *cis*-2-butene was gently removed, the residue was transferred to a vial, and the photolysis tube was washed with ether. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry.

Photolysis of the Twisted Amide Tosylhydrazone Salt in a *trans*-2-Butene and *trans*-1,2-Dichloroethylene Mixture. *trans*-1,2-Dichloroethylene (3 mL, 0.039 mol) was added to a photolysis tube containing the twisted amide tosylhydrazone salt (30 mg, 0.078 mmol). The mixture was cooled with liquid nitrogen and degassed under vacuum. Then *trans*-2-butene (1.0 g, 0.032 mol) was transferred into the photolysis tube by condensation at liquid nitrogen temperature. The sample was degassed three times and irradiated for 4 h at room temperature. The *trans*-2-butene was gently removed, the residue was transferred to a vial, and the photolysis tube was washed with ether. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry.

Adamantanone Tosylhydrazone.[21] THF was distilled over sodium before use. The glassware was oven-dried overnight and cooled in the desiccator over P_2O_5 for a day. To a stirring solution of admantanone (0.15 g, 1 mmol) in 50 mL of dry THF was added *p*-toluenesulfonylhydrazide (97%, 0.2 g, 1.1 mmol) in one portion. After mixing, the solution was stirred at room temperature under argon overnight. A white precipitate was obtained. Crude adamantanone tosylhydrazone was recrystalized from ethanol to give 0.228 g of product (85%), mp 178−180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.02 (br s, 1H), 2.56 (br s, 1H), 2.42 (s, 3H), 1.9 (m, 7H), 1.8 (br s, 2H), 1.7 (d, J = 11.0 Hz, 2H), 1.6 (d, J = 11,0 Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 170.46, 143.78, 135.64, 129.54, 128.06, 39.44, 39.37, 337.71, 36.26, 31.49, 27.62, 21.7; HRMS (EI) calcd for $C_{17}H_{22}N_2O_2S$ 318.14020, found 318.14073.

Adamantanone Tosylhydrazone Salt.[21] The glassware was oven-dried and THF was dried over Na before use. Freshly opened NaH (powder, 95%, 1.2 equiv) was weighed into a round-bottomed flask capped with a septum. The tosylhydrazone was dissolved in a minimum amount of dry THF and transferred to the round-bottomed flask with a syringe. After the deprotonation was complete, THF was removed by an argon flow and the resulting tosylhydrazone salt was available for use in the following photolysis.

Photolysis of Adamantanone Tosylhydrazone Salt in Cyclohexene. Cyclohexene was distilled over $AlCl_3$ before use. Cyclohexene (7−8 mL) was added to the photolysis tube containing adamantanone tosylhydrazone salt (20 mg, 0.062 mmol). The mixture was irradiated for 6 h at room temperature. At the end, the solution was transferred to a vial and the photolysis tube was washed with ether. The organic solutions were combined and concentrated. GC-mass spectrometric analysis showed the cyclopropane adduct as the primary product.

Adamantanone Diaziridine. Adamantanone (1.05 g) was stirred with ammonia in methanol (25% w/v) for 45 min at −10 °C. One gram of freshly prepared hydroxylamine-*O*-sulfonic acid in 10 mL of methanol was added dropwise. The mixture was stirred for 18 h at 4 °C and the solvent was removed by evaporation. The solid residue was extracted with methylene chloride (2 × 20 mL). The combined CH_2Cl_2 extracts were then extracted with 2 N H_2SO_4 at 4 °C (3 × 20 mL). The aqueous extracts were made alkaline with 2 N NaOH at 4 °C. The product was extracted back into CH_2Cl_2, and was then dried over K_2CO_3, filtered, and roto-evaporated to give 1.34 g of diaziridine (82%). The diaziridine was used in the next step without further purification: ^{1}H NMR (500 MHz, C_6D_6) δ 2.0 (d, J = 12.0 Hz, 2H), 1.94 (br s, 2H), 1.8 (m, 9H), 1.7 (br s, 2H), 1.27 (br s, 2H); ^{13}C NMR (500 MHz, C_6D_6) δ 63.6, 38.72, 37.16, 36.45, 35.83, 27.05.

Adamantanone Diazirine. Adamantanone diaziridine (100 mg, 0.609 mmol) was partly dissolved in acetone (5 mL). A solution of CrO_3 (95 mg) in 2 N H_2SO_4 (1.1 mL) was added dropwise at 0 °C with vigorous stirring over 20 min. The solution was then stirred at room temperature for 40 min. The mixture was poured onto ice and the precipitated product was extracted into pentane. The combined pentane solutions were washed sequentially with H_2O (20 mL), 5% Na_2CO_3 (10 mL), and H_2O again, then dried over Na_2SO_4. The solvent was evaporated and further purification was done on a short silica column (pentane elution, 90% yield): ^{1}H NMR (500 MHz, C_6D_6) δ 1.9 (d, J = 13.0 Hz, 4H), 1.72 (br s, 2H), 1.51 (br s, 2H), 1.4 (d, J = 13.0 Hz, 4H), 0.45 (br s, 2H); ^{13}C NMR (500 MHz, C_6D_6) δ 39.35, 37.3, 35.706, 35.28, 28.31; IR (cm^{-1}) 2915, 2850, 1570, 1449, 1260, 1078, 1014.

Photolysis of Adamantanone Tosylhydrazone Salt in *cis*-2-Butene. Adamantanone tosylhydrazone salt (20 mg, 0.062 mmol) was put in a photolysis tube and the tube was degassed under vacuum. *cis*-2-Butene (10 mL) was condensed in at liquid nitrogen temperature. The clear solution was degassed three times and irradiated for 8 h at room temperature. The *cis*-2-butene was gently removed at the end of the reaction and the photolysis tube was rinsed twice with pentane. The combined pentane solutions were concentrated and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (pentane eluent): ^{1}H NMR (500 MHz, C_6D_6) δ 1.91 (br s, 2H), 1.86 (d, J = 13.0 Hz, 2H), 1.76 (br s, 2H), 1.68 (br s, 4H), 1.66 (d, J = 13.0 Hz, 2H), 1.42 (br s, 1H), 0.91 (d, J 6.0 Hz, 6H), 0.46 (br s, 1H), 0.4 (m, 2H); ^{13}C NMR (500 MHz, C_6D_6) δ 42.1,40.08, 38.0, 36.53, 36.43, 29.0, 20.5, 7.8, 1.8; HRMS (EI) calcd for $C_{14}H_{22}$ 190.17215, found 190.17311.

Photolysis of Adamantanone Tosylhydrazone Salt in *trans*-2-Butene. Adamantanone diazirine (20 mg, 0.123 mmol) was put in the photolysis tube and the tube was degassed under vacuum. *trans*-2-Butene (10 mL) was condensed in at liquid N_2 temperature. The clear solution was

degassed three times and irradiated for 8 h at room temperature. The *trans*-2-butene was gently removed at the end of the reaction and the photolysis tube was rinsed with pentane. The pentane solutions were concentrated and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (pentane eluent): ^{1}H NMR (500 MHz, C_6D_6), 1.95 (br s, 2H), 1.82 (dd, J = 13.0 Hz, 4H), 1.62−1.9 (m, H), 1.18 (br s, 2H), 1.4 (m; 6H), 0.1 (m, J = 2H); ^{13}C NMR (500 MHz, C_6D_6) δ 38.09,37.48, 37.34, 34.86, 33.60, 29.017, 25.92, 13.31; HRMS (EI) calcd for $C_{14}H_{22}$ 190.17215, found 190.17234.

Photolysis of Adamantanone Diazirine in *cis*-1,2-Dichloroethylene. Photolysis of adamantanone tosylhydrazone salt in *cis*-1,2-dichloroethylene did not give the expected cyclopropane adduct for some unknown reason. Adamantanone diazirine was photolyzed instead. Adamantanone diazirine (20 mg, 0.123 mmol) was put in the photolysis tube. *cis*-1,2-Dichloroethylene (10 mL) was added. The clear solution was degassed three times and irradiated for 8 h at room temperature. The solution was transferred to another vial, and the tube was rinsed twice with pentane. IThe organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (pentane eluent): ^{1}H NMR (500 MHz, C_6D_6) δ 2.44 (s, 2H), 2.0 (br s,1 H), 1.84 (d, J = 13.0 Hz, 2H), 1.7 (br s, 2H), 1.57 (dd, J = 13.0 Hz, J = 2.0 Hz, 2H), 1.52 (d, J = 13.0 Hz, 2H), 1.46 (d, J = 13.0 Hz, 2H), 1.57 (dd, J = 13.0 Hz, J = 2.0 Hz, 2H), 0.24 (br s,1 H); ^{13}C NMR (500 MHz, C_6D_6) δ 42.23, 37.68, 36.96, 35.47, 35.21, 34.39, 28.73, 27.94. The exact mass could not be measured because the parent peak was missing.

Photolysis of Adamantanone Diazirine in *trans*-1,2-Dichloroethylene. Adamantanone diazirine (20 mg, 0.123 mmol) was put in the photolysis tube. *trans*-1,2-Dichloroethylene (10 mL) was added. The clear solution was degassed three times and irradiated for 8 h at room temperature. The solution was transferred to another vial and the tube was rinsed twice with pentane. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (pentane eluent): ^{1}H NMR (500 MHz, C_6D_6) δ 2.66 (s, 2H), 1.70 (d, J = 12.0 Hz, 2H), 1.65 (m, 2H), 1.45 (br s, 6H), 1.42 (d, J = 12.0 Hz, 2H), 1.27 (br s, 2H); ^{13}C NMR (500 MHz, C_6D_6) δ 46.05, 38.03, 37.06, 36.28, 35.64, 33.42, 27.9. The exact mass could not be measured because the parent peak was missing.

Photolysis of Adamantanone Diazirine in 1,1-Dichloroethylene. The same procedure and workup was used as described for photolysis of adamantanone diazirine in *trans*-1,2-dichloroethylene. The reaction mixture was analyzed by GC-mass spectrometry. The cyclopropane adduct was further purified by preparative TLC (pentane eluent, obtained 20 mg, yield 70%): ^{1}H NMR (500 MHz, C_6D_6) δ 2.67 (d, J = 12.0 Hz, 2H), 2.02 (s, 2H), 1.8 (br s,1 H), 1.5 (br s, 2H), 1.48 (br s,1 H), 1.42 (d, J = 12.0 Hz, 2H), 1.40 (d, J = 12.0 Hz, 2H), 1.34 (br s, 2H), 1.09 (br s, 2H); ^{13}C NMR (500 MHz, C_6D_6) δ 50.45, 38.0, 37.53, 35.62, 34.16, 28.01, 27.08; HRMS (EI) calcd for $C_{12}H_{16}Cl_2$ 230.06290, found 230.06261.

Photolysis of Adamantanone Diazirine in *cis*-2-Butene and *cis*-1,2-Dichloroethylene. *cis*-1,2-Dichloroethylene (2.8 mL, 0.037 mol) was added to a photolysis tube containing adamantanone diazirine (20 mg, 0.123 mmol). The mixture was chilled with liquid nitrogen and was degassed under vacuum. Then *cis*-2-butene (1.8 g, 0.032 mol) was condensed into the photolysis tube. The sample was degassed three times and irradiated for 8 h at room temperature. The *cis*-2-butene was gently removed, the residue was transferred to a vial, and the photolysis tube was washed with pentane. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry.

Adamantanone Diazirine Photolysis in *trans*-2-Butene and *trans*- 1,2-Dichloroethylene. *trans*-1,2-Dichloroethylene (2.8 mL, 0.037 mol) was added to a photolysis tube containing adamantanone diazirine (20 mg, 0.123 mmol). The mixture was chilled with liquid nitrogen and degassed under vacuum. Then *trans*-2-butene (1.8 g, 0.032 mol) was condensed into the photolysis tube. The sample was degassed three times and irradiated for 8 h at room temperature. Then the *trans*-2-butene was gently removed, the residue was transferred to a vial, and the photolysis tube was washed with pentane. The organic solutions were combined, concentrated, and analyzed by GC-mass spectrometry.

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