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SHORT COMMUNICATION

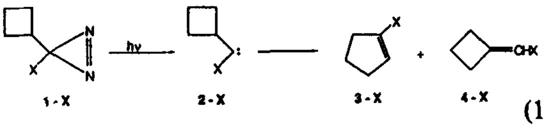
CARBON AND HYDRIDE MIGRATIONS OF CYCLOBUTYLHALOCARBENES

ROBERT A. MOSS* AND GUO-JIE HO

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, USA

The photolysis of cyclobutylchlorodiazirine affords chlorocyclopentene and chloromethylenecyclobutane by direct rearrangements from the diazirine's excited state (65%) and by competitive formation and subsequent rearrangement of cyclobutylchlorocarbene. The involvement of excited diazirine in the analogous cyclobutylfluorodiazirine photolysis is much reduced (12%).

We recently reported[1] that the photolysis of cyclobutylchlorodiazirine (**1**-Cl) afforded chlorocyclopentene (**3**-Cl) and chloromethylenecyclobutane (**4**-Cl) by competitive 1,2-C and 1,2-H shifts that were attributed to the intermediate cyclobutylchlorocarbene, **2**-Cl:



(1)

The **3**-Cl/**4**-Cl product ratio of 2·17 at 21 °C, coupled with a laser flash photolysis study led to assignments of absolute rate constants of $4\cdot6\times10^{7}\,\mathrm{s}^{-1}$ (~C) and $2\cdot1\times10^{7}\,\mathrm{s}^{-1}$ (~H) to the competitive processes. A parallel examination of cyclobutylfluorocarbene (**2**-F) gave the **3**-F/**4**-F product ratio as 3·4 (23 °C), with $k_C = 1\cdot8\times10^{6}\,\mathrm{s}^{-1}$ and $k_H = 5\cdot3\times10^{5}\,\mathrm{s}^{-1}$.[2]

However, strong kinetic evidence has accumulated that the 1,2-H shifts frequently observed in the reactions of alkyl- and alkylhalocarbenes are composite processes that include hydride shifts of both the carbene and a second transient.[3–5] Moreover, the trappable yields of several alkylchlorocarbenes, formed on photolysis of alkylchlorodiazirine precursors, correlate with the α-CH bond dissociation energies (BDE) of the alkyl groups.[5] Thus, a high BDE (e.g. R = Me in Me—C—Cl) leads to more carbene, as measured by the optical yield of the ylide formed when the carbene is captured by pyridine, but a low BDE (R = *i*-Pr in *i*-Pr—C—Cl) results in much less carbene and ylide, even though the yield of ~H product is substantial. Much of this latter process is attributed to a hydride shift, concerted with nitrogen loss, that occurs in the excited state of the diazirine precursor, in direct competition with the simple nitrogen loss that affords the carbene.[5]

When there is no α-H in the carbene's alkyl group (R = *t*-Bu), or the α-H BDE is very high (R = cyclopropyl), almost all of the excited-state precursor affords the carbene; a high yield of carbene–pyridinium ylide is observed, and there is little competitive rearrangement.[5] Finally, White and Platz[5] observed 'no evidence for carbon migration in the excited states of alkylchlorodiazirines.' This process was judged less efficient than ~H, at least with 'simple' alkylchlorodiazirines.

Here we describe a further investigation of the cyclobutylchlorodiazirine/cyclobutylchlorocarbene system[1] (not examined by White and Platz[5]) that reveals extensive excited-state diazirine contributions to both ~C and ~H products. Olefinic interception of the carbene permits us to dissect the intramolecular reaction into excited-state and carbene components. Additionally, we find the excited-state diazirine pathway to be much more important in the alkylchloro system, **1**-Cl/**2**-Cl, than in the corresponding fluoro case, **1**-F/**2**-F.

RESULTS

We photolyzed pentane solutions of **1**-Cl[1,6] (20 °C, $A_{345} \approx 1\cdot0$), together with various amounts of tetramethylethylene or trimethylethylene, using a

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[*] Author for correspondence.

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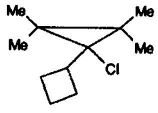
200 W focused Osram XE UV lamp ($\lambda > 320$ nm) until the diazirine had been destroyed. Capillary gas chromatographic (GC) analysis on a dimethylpolysiloxane column revealed the presence of the known[1,6] ~C and ~H rearrangement products, **3**-Cl and **4**-Cl, in addition to the previously synthesized[6] intermolecular addition products, **5** or **6**, from tetramethylethylene or trimethylethylene, respectively. The identities of the addition products were further substantiated by GC–mass spectrometry (MS). Normalized product distributions are shown in Tables 1 and 2 as a function of alkene concentrations.

Parallel experiments were carried out with cyclobutylfluorodiazirine, **1**-F.[2] Photolysis as above of **1**-F, in the presence of various amounts of 2-methylbut-1-ene, gave mixtures of the known[2] intramolecular ~C and ~H products, **3**-F and **4**-F, in addition to the isomeric intermolecular addition products, **7**. The latter were characterized by ^{1}H and ^{19}F NMR and GC–MS (M$^+$).[3] These product distributions are presented graphically in Figure 2 and will be discussed below.



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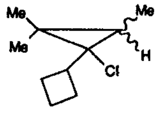

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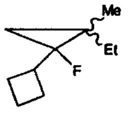

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DISCUSSION

In the cyclobutylchloro system, the ratio of addition (Ad) to rearrangement (Re) product yields increases with either alkene trap, tetramethylethylene (Table 1 and Figure 1A) or trimethylethylene (Table 2 and Figure 1C). However, both of these correlations are strongly curved, behavior that is inconsistent with a simple competitive mechanism in which a single reactive intermediate (e.g. carbene **2**-Cl) partitions between addition to the alkene and intramolecular rearrangement. Such a mechanism would exhibit a linear dependence of Ad/Re on [alkene].[3,4]

In contrast, we find the inverse correlations of Re/Ad vs 1/[alkene] to be linear with either alkene (see Tables 1 and 2 and Figures 1B and 1D). These relationships are in accord with the mechanistic scheme outlined in

Table 1. Photolysis of cyclobutylchlorodiazirine in tetramethylethylene–pentane

[$\mathrm{Me_2C{=}CMe_2}$] (M)	Rearr. (%)[a]	**5** (%)	**3**-Cl/**4**-Cl	1/[$\mathrm{Me_2C{=}CMe_2}$]	**5**/rearr.[a]	Rearr./**5**[a]
0	100	0	2·23	–	0	–
0·084	98·3	1·7	2·17	11·9	0·0173	57·8
0·168	97·1	2·9	2·13	5·95	0·0299	33·5
0·335	94·7	5·3	2·09	2·99	0·0560	17·9
0·670	90·5	9·5	2·04	1·49	0·105	9·53
1·34	85·3	14·7	1·94	0·746	0·172	5·80
2·35	78·6	21·4	1·82	0·426	0·272	3·67
3·35	74·8	25·2	1·76	0·298	0·337	2·97
5·03	71·3	28·7	1·70	0·198	0·403	2·48
6·67	68·5	31·5	1·63	0·150	0·460	2·17

[a] Rearr. refers to the sum of 3-Cl and 4-Cl.

Table 2. Photolysis of cyclobutylchlorodiazirine in trimethylethylene–pentane

[$\mathrm{Me_2C{=}CHMe_2}$] (M)	Rearr. (%)[a]	**6** (%)	**3**-Cl/**4**-Cl	1/[$\mathrm{Me_2C{=}CHMe_2}$]	**6**/rearr.[a]	Rearr./**6**[a]
0	100	0	2·23	–	0	–
0·094	98·3	1·7	2·18	10·6	0·0173	57·8
0·189	96·8	3·2	2·13	5·29	0·0330	30·3
0·378	93·9	6·1	2·08	2·65	0·0650	15·4
0·755	89·8	10·2	2·02	1·32	0·114	8·80
1·51	83·8	16·2	1·90	0·662	0·193	5·17
2·64	78·4	21·6	1·80	0·378	0·276	3·63
3·78	74·6	25·4	1·71	0·264	0·340	2·94
5·66	71·6	28·4	1·64	0·176	0·400	2·52
7·55	67·6	32·4	1·57	0·132	0·479	2·09

[a] Rearr. refers to the sum of 3-Cl and 4-Cl.

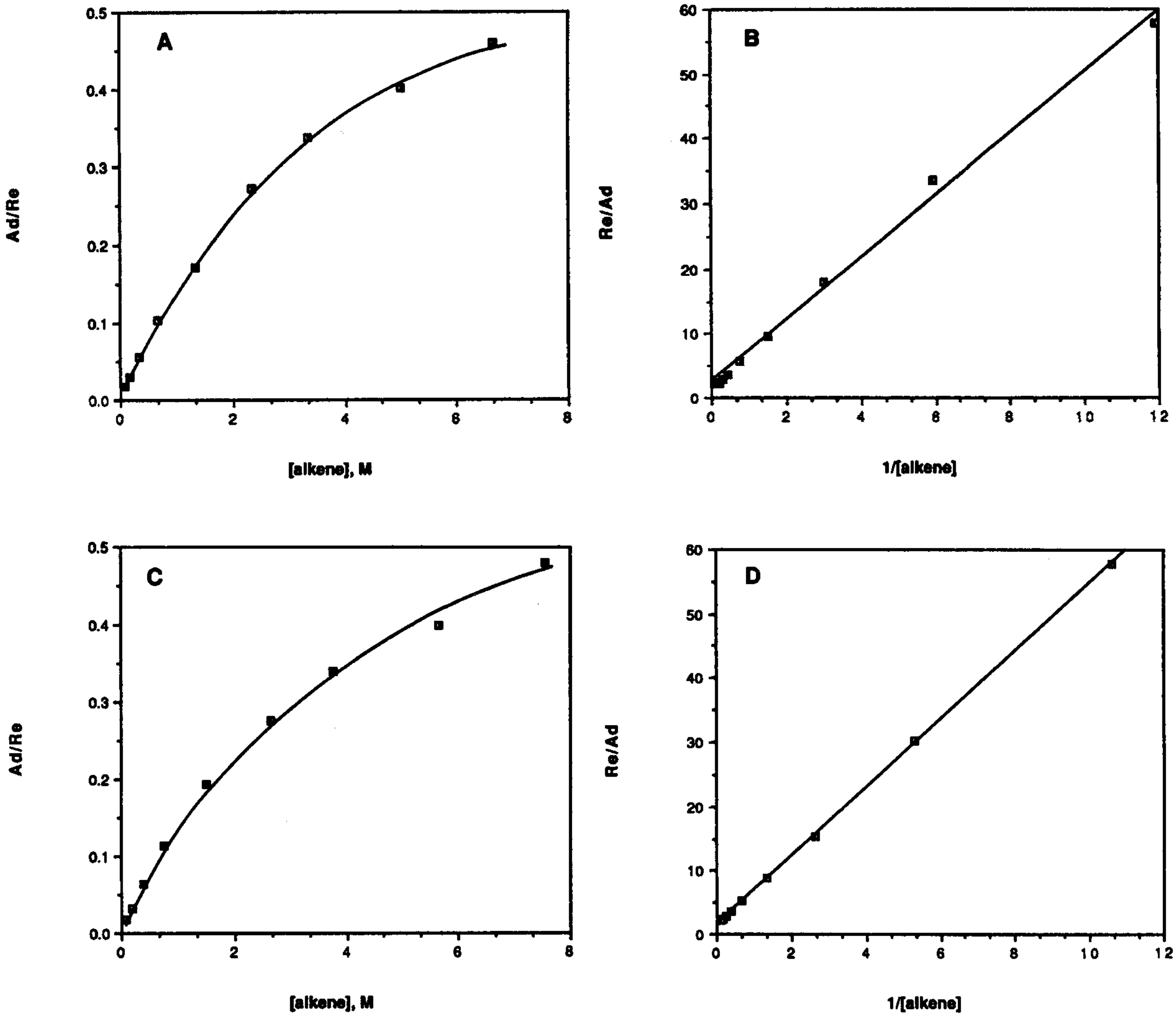
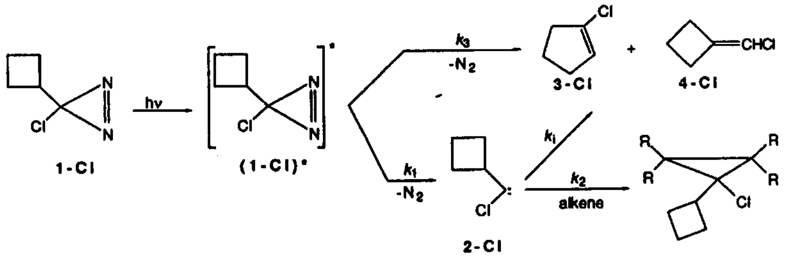


Figure 1. (A) Addition to rearrangement product ratio, [5]/[3-Cl + 4-Cl], vs [alkene] for the photolysis of 1-Cl in tetramethylethylene (cf. Table 1). (B) Rearrangement to addition product ratio, [3-Cl + 4-Cl]/[5], vs 1/[alkene] for the photolysis of 1-Cl in tetramethylethylene (cf. Table 1). (C) Addition to rearrangement product ratio, [6]/[3-Cl + 4-Cl], vs [alkene] for the photolysis of 1-Cl in trimethylethylene (cf. Table 2). (D) Rearrangement to addition product ratio, [3-Cl + 4-Cl]/[6], vs 1/[alkene] for the photolysis of 1-Cl in trimethylethylene (cf. Table 2)



(2)

equation (2),[4] where we introduce a second product-forming intermediate, the excited diazirine (**1**-Cl)*. The key feature of this mechanism is that the excited diazirine not only gives the carbene (k_1) but also directly affords the 1,2 ~ C and 1,2 ~ H products (k_3). The carbene either rearranges to the intramolecular products (k_i), or adds to the alkene (k_2).

In fact, *any* second product-forming intermediate could satisfy the kinetic observations; a carbene–alkene complex[3,7] or an excited carbene[8] are also candidates. At present, however, in accord with the recent work of White and Platz,[5] we prefer the excited diazirine mechanism for reasons of economy.

The analytical expression corresponding to the mechanism of equation (2) is given in equation (3) where Re represents the intramolecular rearrangement products, **3**-Cl and **4**-Cl, and Ad is the intermolecular cyclopropane adduct.

$$\mathrm{Re}/\mathrm{Ad} = k_3/k_1 + [k_i(k_1 + k_3)]/k_1k_2[\text{alkene}] \qquad (3)$$

According to equation (3), the Y-intercepts of the correlations in Figures 1B and 1D represent the ratio of rate constants (k_3/k_1) for the direct rearrangements (with nitrogen loss) of (**1**-Cl)* to **3**-Cl or **4**-Cl (where k_3 is the sum of k_c and k_H), relative to the simple nitrogen-loss conversion of (**1**-Cl)* into carbene **2**-Cl, from which the rearrangement products also arise.

The observed Y-intercepts are 2·18 ± 0·57 for tetramethylethylene ($r = 0{\cdot}997$, Figure 1B) and 1·61 ± 0·12 for trimethylethylene ($r = 1{\cdot}00$, Figure 1D). Although the agreement is not particularly good, the differences are within the combined standard errors, and the implication of a second reactive intermediate to products **3**-Cl and **4**-Cl is secure. Indeed, the experimental k_1/k_3 ratios translate into 68% excited diazirine incursion (Figure 1B) or 62% excited diazirine (Figure 1D), leading to an 'average' value of 65% of excited diazirine and 35% of carbene parentage for **3**-Cl and **4**-Cl.

Note that at the highest employed concentrations of tetramethylethylene (6·67 M, Table 1) or trimethylethylene (7·55 M, Table 2), where the carbene should be very largely diverted to adduct **5** or **6**, and the rearrangement products should stem almost exclusively from excited diazirine, the observed ratio of rearrangement to addition products is *ca* 68 : 32, very similar to the 'average' partition derived from the Y-intercepts of Figures 1B and 1D. This provides good evidence for the validity of the kinetic analysis.

Moreover, it seems an inescapable conclusion that much of the ~C and ~H products, formed on photolysis of diazirine **1**-Cl, comes not from carbene **2**-Cl, but rather in the Goodman–Platz formulation,[4,5] from the excited diazirine. In this light, we can refine the absolute rate constants that were previously offered for the ~C and ~H reactions of the carbene.[1]

The overall rate constant for carbene rearrangement, $6{\cdot}8 \pm 0{\cdot}5 \times 10^7\ \mathrm{s}^{-1}$ (21 °C),[1] was derived from a laser flash photolysis study of the kinetics of ylide formation[9] between carbene **2**-Cl and pyridine; it is independent of excited diazirine intervention. From Tables 1 and 2 at the highest alkene concentration, we take 1·60 ± 0·03 as the **3**-Cl/**4**-Cl (~C/~H) ratio due only to excited diazirine rearrangement. On the other hand, at [alkene] = 0, the observed **3**-Cl/**4**-Cl ratio of 2·23 represents a 65 : 35 blend of excited diazirine and carbene rearrangements (see above). A **3**-Cl/**4**-Cl or ~C/~H ratio of *ca* 4·8 for the rearrangements of carbene **2**-Cl satisfies these constraints.

With the latter product ratio, and the absolute rate constant $(k_c + k_H) = 6{\cdot}8 \times 10^7\ \mathrm{s}^{-1}$ for total carbene rearrangement, we obtain $k_c = 5{\cdot}6 \times 10^7\ \mathrm{s}^{-1}$ and $k_H = 1{\cdot}2 \times 10^7\ \mathrm{s}^{-1}$ for the individual ~C and ~H rearrangements of carbene **2**-Cl. We estimate ±10% errors in these values. They can be compared with $k_c = 4{\cdot}6 \times 10^7\ \mathrm{s}^{-1}$ and $k_H = 2{\cdot}1 \times 10^7\ \mathrm{s}^{-1}$, the previously offered[1] rate constants that were derived without consideration of the excited diazirine contribution to these rearrangements. It is perhaps amusing that despite the extensive contribution of the excited-state pathway, the revised rate constants are not very different from the earlier values. It is likely that the differential activation parameters for 1,2-C and 1,2-H shifts of carbene **2**-Cl, previously obtained from the variation of **3**-Cl/**4**-Cl with temperature,[1] require little revision.

Why is the ~C process important in the chemistry of the excited cyclobutylchlorodiazirine (**1**-Cl)* but seemingly unimportant with excited cyclopropylchlorodiazirine?[5] Platz[10] suggests that at least part of the difference can be found in the comparative relief of ring strain that attends each ~C process. The conversion of cyclopropylchlorodiazirine into chlorocyclobutene[11] would increase ring strain by *ca* 2 kcal mol^{-1} (1 kcal = 4·184 kJ), whereas the conversion of **1**-Cl into chlorocyclopentene would decrease this component by *ca* 20 kcal mol^{-1}.[12] Thus, excited cyclopropylchlorodiazirine eschews ring expansion/nitrogen loss in favor of simple nitrogen loss to the carbene, which is more exothermic. With excited diazirine (**1**-Cl)*, however, ring expansion/nitrogen loss should be more exothermic than carbene-forming nitrogen loss alone owing to the added strain energy release. Accordingly, the ensuing kinetic competition favors the ring expansion by *ca* 2 : 1. Although this argument appears plausible, it seems incomplete. For example, it does not account for the ~H shift of (**1**-Cl)* to **4**-Cl, which does not relieve strain, but still competes effectively with the ~C process (see above).

To save space, our results with cyclobutylfluorocarbene, **2**-F, are presented in graphical form only. We again correlated the GC-determined product distributions as a function of added alkene. The data are presented as correlations of Ad/Re vs [alkene] in Figure 2A and as Re/Ad vs 1/[alkene] in Figure 2B.

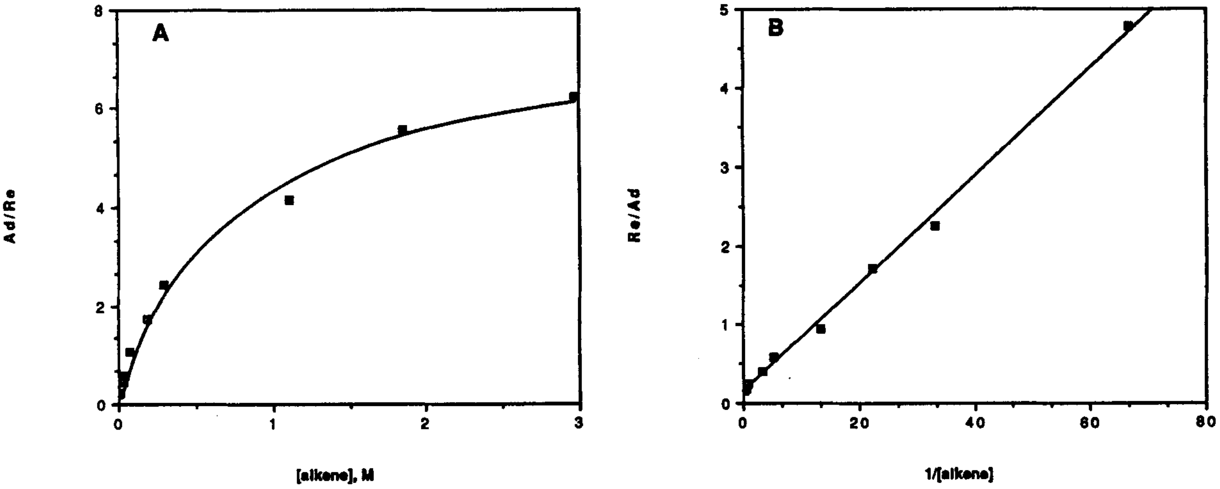


Figure 2. (A) Addition to rearrangement product ratio, [7]/[3-F + 4-F], vs [alkene] for the photolysis of 1-F in 2-methylbut-1-ene. (B) Rearrangement to addition product ratio, [3-F + 4-F]/[7], vs 1/[alkene] for the photolysis of 1-F in 2-methylbut-1-ene

As we observed with **1**-Cl/ **2**-Cl, so too with the **1**-F/**2**-F system, the Ad/Re vs [alkene] correlation is strongly curved. However, the inverse correlation (Figure 2B) is linear ($r = 0{\cdot}998$), with a Y-intercept of $0{\cdot}14 \pm 0{\cdot}04$ that corresponds to a 12% incursion of excited diazirine (**1**-F)* in the formation of products **3**-F and **4**-F. The previously offered[2] $\sim$C/$\sim$H ratio of 3·4, attributed solely to carbene **2**-F, would increase only to 4·2 upon algebraic 'removal' of the excited diazirine contribution. This small correction leads to insignificant changes in the published[2] k_c and k_H rate constants for the rearrangements of carbene **2**-F.

What is noteworthy, however, is the much lower incursion of excited diazirine rearrangements in the **1**-F photolysis (12%) compared with the **1**-Cl photolysis (65%). An attractive rationalization is that carbene **2**-F is more stable than **2**-Cl because of the greater resonance electron donation available from its fluorine substituent.[2] Therefore, the corresponding excited diazirines will partition more toward carbene formation, and away from direct rearrangement, in the case of (**1**-F)*.

This behavior may be general; similar phenomena were observed in the course of an isotope effect study of the neopentylhalodiazirines. Thus, photolysis of neopentylfluorodiazirine led to *ca* 94% of product formation from the carbene, accompanied by *ca* 6% of direct $\sim$H rearrangement from the excited diazirine,[13] whereas in the photolysis of neopentylchlorodiazirine, carbene formation fell to *ca* 60% while product formation from the excited diazirine rose to *ca* 40%.[14]

CONCLUSIONS

The photolysis of cyclobutylchlorodiazirine (**1**-Cl) affords chlorocyclopentene (**3**-Cl) and chloromethylenecyclobutane (**4**-Cl) by competing pathways. The major route (65%) most likely involves direct rearrangement, coupled with loss of nitrogen, from excited diazirine (**1**-Cl)*. The minor product-forming pathway (35%) involves nitrogen loss from (**1**-Cl)*, affording cyclobutylchlorocarbene (**2**-Cl), which subsequently undergoes $\sim$C and $\sim$H rearrangements to **3**-Cl and **4**-Cl, respectively. The absolute rate constants for the latter reactions are $k_c = 5{\cdot}7 \times 10^7\ \mathrm{s}^{-1}$ and $k_H = 1{\cdot}1 \times 10^7\ \mathrm{s}^{-1}$. Photolysis of the corresponding cyclobutylfluorodiazirine (**1**-F), in contrast, involves much less direct product formation from the excited diazirine (12%); products **3**-F and **4**-F are very largely derived (88%) from carbene **2**-F.

ACKNOWLEDGEMENTS

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