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Intermolecular Chemistry Of A Cyclopropylcarbene And Its Mechanistic Implications

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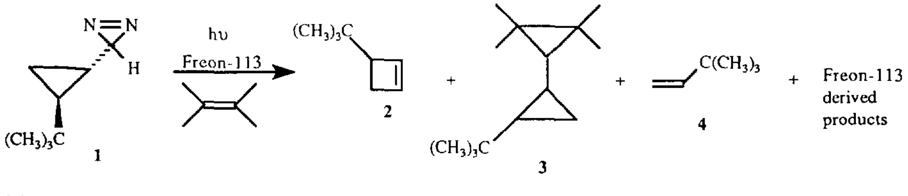
Abstract: *Trans*-3-(2-*tert*-butylcyclopropyl)-3*H*-diazirine was decomposed both thermally (100 °C) and photochemically (350 nm, -25 to 25 °C) to give the anticipated ring-expanded 3-*tert*-butylcyclobutene product (50% photochemical, 64% thermal), along with azine and products of trapping by solvent. In the presence of tetramethylethylene (TME), a bicyclopropyl adduct was formed in yields as high as 37% (thermal) or 32% (photochemical). The yield of 3-*tert*-butylcyclobutene product, however, is only very slightly (0-7%) decreased upon increasing the concentration of TME. Similar results were obtained with propylamine as the carbene trapping agent. The response of the product mixture to changes in the concentration of the trapping agent shows that there are two product-forming pathways. The mechanistic implications of these observations are discussed.

Several laboratories, including our own, are interested in measuring the lifetimes of simple alkyl, dialkyl and cycloalkylcarbenes in fluid solution. These studies have demonstrated that simple carbenes are relatively long lived [1] and should have useful intermolecular chemistry in addition to rearrangement chemistry.[2]

Our reported laser flash photolysis studies of cyclopropylcarbene indicated that this carbene has a lifetime in hydrocarbon solution of 20 ns at ambient temperature which is controlled, at least in part, by reaction with solvent.[3] Thus, cyclopropylcarbene should be sufficiently long lived, as is chlorocyclopropylcarbene,[4] to achieve bimolecular trapping chemistry in significant yields. This has prompted the present study of the bimolecular chemistry of *trans*-2-*tert*-butylcyclopropylcarbene.

Pyrolysis (100°C) or photolysis (350 nm, 25°C) of *trans*-3-(2-*tert*-butylcyclopropyl)-3*H*-diazirine **1** in $CF_2ClCFCl_2$ (Freon-113) induces the ring expansion reaction discovered in the parent cyclopropylcarbene system by Friedman and Shechter.[5] Cyclobutene **2** is produced in 44-64% yield, along with a complex mixture of halogenated compounds and a small amount of *tert*-butylethylene **4** (Tables 1 and 2). When **1** is decomposed in Freon-113 containing 2,3-dimethyl-2-butene (TME), adduct **3** is also produced in yields as high as 26-37%. The yield of **3** smoothly increases as the concentration of TME increases (Tables 1 and 2).



The critical observation is that the concentration of TME depresses the absolute yield of **2** formed on thermal (100 °C, Table 1) or photochemical (350 nm, 25 °C, Table 2) decomposition of **1** by less than 7%. At lower temperatures (0 °, -25 °C) there is **no** decrease in the yield of cyclobutene **2** in the presence of TME. Therefore, **2** and **3** cannot issue from a common precursor. There must be two product-forming pathways. Similar results were obtained when propylamine was used as the trap. Unlike TME, propylamine cannot undergo a dipolar cycloaddition reaction with putative diazo intermediate **5**, to form an adduct (6) without the intervention of a carbene intermediate.

Table 1. Absolute Product Yields in the Pyrolysis of **1** in $CF_2ClCFCl_2$ (100 °C) as a Function of the Concentration of TME.

TME (M)	%2	%3	%4
0.0	64	0	14
0.036	64	4.9	13
0.067	65	8.7	12
0.135	64	14	10
0.261	64	20	8.4
0.506	60	26	6.6
0.948	57	32	3.9
1.94	57	37	3.2

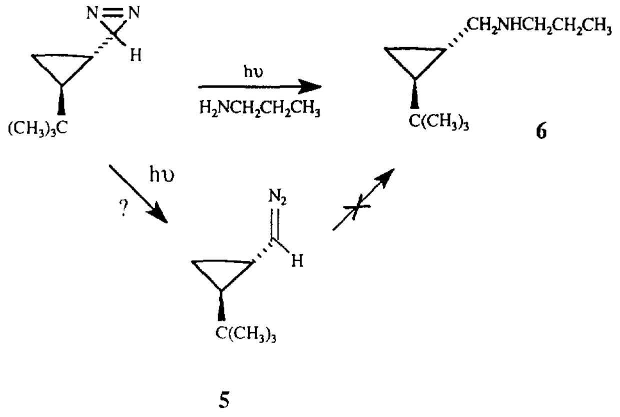


Table 2. Absolute Product Yields in the Photolysis (350 nm) of **1** in $CF_2ClCFCl_2$ (-25 °C, 0 °C and 25 °C) as a Function of the Concentration of TME.

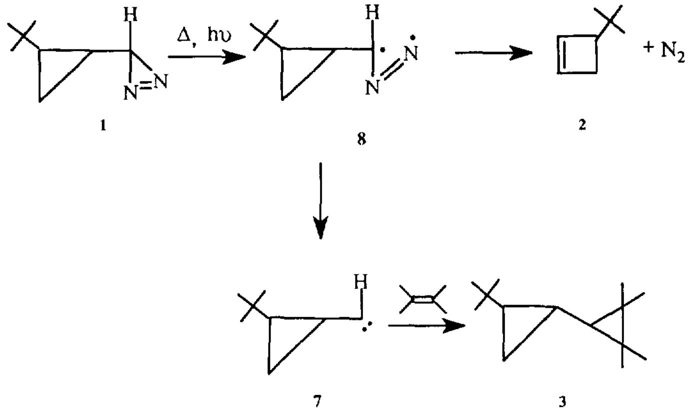
	-25 °C			0 °C			25 °C		
TME (M)	%2	%3	%4	%2	%3	%4	%2	%3	%4
0							50	0	20
0.017	44	13	10	46	10	13	49	7	15
0.034	47	19	10	44	14	12	46	10	14
0.067	45	22	10	46	20	13	43	15	15
0.134	46	26	11	48	24	13	47	22	13
0.269	45	30	11	45	27	12	43	24	14
0.420	46	32	10	47	28	13	46	27	13

Table 3. Absolute Product Yields in the Photolysis (350 nm) of **1** in Pentane (25 °C) as a Function of the Concentration of Propylamine.

n-propylamine (M)	% 2	% 6	% 4
0	56	0	5.0
0.061	52	20	4.8
0.120	52	26	4.8
0.243	48	27	4.6
0.486	50	26	5.2
0.973	47	30	4.4
1.52	49	27	4.9

The need for two product-forming intermediates in the decomposition of diazirines, was first discussed by Frey over 30 years ago.[6] Numerous subsequent studies[7] have reached the same conclusion, including that of Moss **et al.**[8] with a closely related chlorocyclopropylcarbene system. Other recent examples include benzylchloro,[11] methylchloro,[12] neopentylchloro,[13] cyclobutylchlorocarbene,[14] and cyclobutanylidene.[15]

What is the second product forming pathway? One can invoke carbene-alkene complexes[11] or a second, untrappable conformation[9a,b] of carbene 7. Nevertheless, we postulate that upon pyrolysis or photolysis, diazirine **1** opens to form diradical **8**. This process is well known in cyclopropene chemistry[16] and is predicted by theory[17] for the photochemical process.



This type of mechanism can also explain the original observations of Frey[6] and those of subsequent investigators,[7,8] who recognized the need for two product forming pathways. According to this mechanism, ring expansion of a cyclopropylcarbene, which is predicted to have an enthalpic barrier, cannot compete in solution with faster intermolecular reactions of the carbene, which generally do not have an enthalpic barrier. Moss[3,8] and Liu[18] were able to study the ring expansion of chlorocyclopropylcarbenes in solution because the chlorine substituent stabilizes the carbene and retards the rate of reaction of the carbene with solvent. In that case, the chlorocyclopropylcarbene is sufficiently long lived to undergo the ring expansion reaction.

Our results confirm the existence of an enthalpic barrier to ring expansion of cyclopropylcarbene.[3,9] The effect of TME on the yield of cyclobutene is greatest at 100 °C demonstrating that the trappable carbene can ring expand at elevated temperatures. As the temperature is lowered, the yield of cyclobutene **2** becomes completely independent of the concentration of TME. At low temperature (-25 °, 0 °C), the ring expansion of carbene **8** can no longer compete with reaction of the carbene with solvent or trapping agent, which likely have no enthalpic barriers to surmount.[10]

The photochemical (-25 °C to +25 °C) fragmentation reaction, which forms *tert*-butylethylene **4**, must proceed via diradical **8** and not carbene **7**, as TME has no effect on the yield of alkene **4**. However, the presence of TME substantially depresses the yield of alkene **4** at 100 °C demonstrating that the carbene can fragment at elevated temperatures. These results again mirror those of Moss *et al*.[8] In general, intramolecular carbene processes, which must overcome enthalpic barriers, can only compete with intermolecular processes, which do not, at elevated temperatures.

Finally we note that these results are in good agreement with new data of Jones and Shevlin.[19] These workers found that non-nitrogenous precursors of "cyclopropylmethylcarbene" give higher ratios of vinylcyclopropane/1-methylcyclobutene than tosylhydrazone salts[5,20] and concluded that ring expansion proceeds in the carbene precursor, rather than the free carbene.

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21. Compound **2** : ^{1}H NMR (CDCl$_3$) d 6.05 (m, 1H), 5.95 (m, 1H), 2.67 (m, 1H), 2.38 (m, 1H), 2.18 (m, 1H), 0.87 (s, 9H); ^{13}C NMR (CDCl$_3$) d 138.907, 135.651, 55.032, 31.977, 31.172, 26.477. Compound **3**: ^{1}H NMR d 1.01 (s, 12H), 0.79 (s, 9H), 0.48 (m, 1H), 0.45 (m, 1H), 0.32 (m, 1H), 0.10 (m, 1H), -0.42 (d, 1H); ^{13}C NMR d 38.856, 30.351, 29.608, 28.841, 28.539, 23.617, 20.846, 20.818, 17.710, 17.407, 9.772, 7.735.
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