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INTERMOLECULAR CHEMISTRY OF A DIALKYLCARBENE: ADAMANTANYLIDENE

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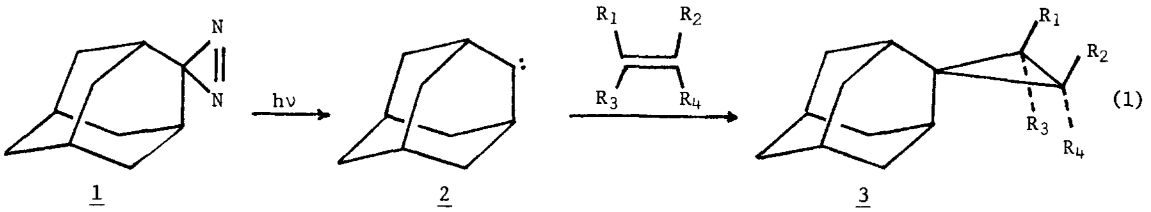
Summary. We describe the C=C addition and C-H insertion reactions of adamantanylidene with various substrates.

Due to their proclivity for intramolecular chemistry, intermolecular reactions of alkylcarbenes (as distinct from organometallic alkylcarbenoids) are uncommon.[1] Exceptions include the low yield additions of methylcarbene to propene[2] and of cyclohexanylidene to alkenes,[3] the formation of iminoxy radicals by additions of (triplet) cyclohexanylidene and dimethylcarbene to NO,[4] and the possible addition of cycloheptanylidene to styrene.[5] There are also reports of alkene addition reactions of cyclopropylidenes, 7-norbornanylidene, and adamantanylidene. 2,2-Diphenylcyclopropylidene, for example, readily adds to alkenes.[6] Cyclopropylidenes exhibit a complicated chemistry, however, and are not typical dialkylcarbenes. Dimethylcarbene would be more representative, but our attempts to detect its low temperature intermolecular addition to isobutene failed.[7] 7-Norbornanylidene seems slow to react intramolecularly because it must afford strained products; it appears to be trappable with alkenes,[8] and its chemistry remains open to investigation.

Alone among representative dialkylcarbenes, adamantanylidene appears to possess a simple, readily accessible, plentiful intermolecular chemistry, ripe for intensive investigation. Pyrolysis of the Li salt of adamantanone tosylhydrazone gave 2,4-dehydroadamantane, attributed to 1,3-intramolecular insertion of adamantanylidene.[9] Formation of this strained hydrocarbon from the carbene is presumably rather "slow," and formation of the anti-Bredt olefin adamantene (by 1,2-hydride migration) is even more difficult,[10] so that intermolecular chemistry is quite competitive. Photolysis or thermolysis of spiro[adamantane-2,3'-diazirine], 1, in hexane or cyclohexane led to C-H insertion products of adamantanylidene, 2,[11] whereas thermolysis of 1 in cyclohexene (200-220°, 6 h) led in 75% yield to a 1:1 mixture of cyclopropanation and insertion products.[12] More recently, 2 has been used to label dioleoyllecithin vesicles by C-H insertion and C=C addition reactions;[13] labeling of proteins within erythrocyte membranes was also reported.[14] We now report a careful study of the elementary intermolecular chemistry of adamantanylidene, which permits, for the first time, assessment of the reactivity of a representative dialkylcarbene.

Adamantanone was converted to spiro[adamantane-2,3'-diaziridine] in 80% yield upon treatment with freshly prepared[15] hydroxylamine-O-sulfonic acid and methanolic ammonia.[14] Oxidation of the diaziridine with CrO_3/H_2SO_4 in acetone gave diazirine 1 (92%, after pentane elution from silica



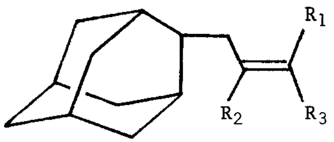
	R_1	R_2	R_3	R_4
(a)	Me	Me	Me	Me
(b)	Me	H	Me	H
(c)	Me	Me	H	H
(d)	Me	H	H	Me
(e)	C_6H_5	H	H	H
(f)	COOMe	H	H	H
(g)	CN	H	H	H

gel), comparable in ir, nmr, and uv properties to the material described by Bayley and Knowles.[14] Photolysis[16] of dilute solutions of 1 in alkenes gave the spirocyclopropanes 3a-3g, eq. (1). In some cases, C-H insertion products, as well as adamantanone azine[11] (removed by filtration of pentane solutions of the crude product mixtures), and small quantities of 2,4-dehydroadamantane[9] and adamantanone, were also formed. Products were isolated by gas chromatography on Carbowax 20M, DC-710, or Apeizon L columns, using appropriate operating temperatures (120°-170°C). Product identities were established by structurally appropriate ^{1}H nmr spectra, as well as mass spectroscopy or elemental analysis.

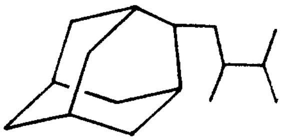
From isobutene and 2, 3b was formed in 42% yield, accompanied by traces (<1%) of insertion product. On the other hand, reaction of 2 with tetramethylethylene gave a number of products, from which cyclopropane 3a and insertion product 4 could be isolated in low yields (<10%). Additions of 2 to *cis*-butene or *trans*-butene were cleaner. From the former substrate we isolated 26% of 3c, accompanied by 1.5% of insertion product 5 (nmr only); whereas, from the latter alkene, we obtained 20% of 3d, accompanied by 3.3% of insertion product 6 (nmr only). Gc analysis of the crude product from *cis*-butene indicated the *absence* of 3d, so that addition of 2 to *cis*-butene is stereospecific, implicating *singlet* 2 as a key reactive intermediate.

Photolysis of 1 in 2,3-dimethylbutane afforded the primary and tertiary C-H insertion products, *7 and 8 in a 1:1.5 ratio.*[17] Statistically corrected, this yields a *tert.*/*prim.* selectivity ratio of 4.0 for C-H insertion of 2 into 2,3-dimethylbutane, which positions adamantanylidene's *tert.*/*prim.* insertion selectivity between those of carboethoxycarbene (2.9) and cyclopentadienylidene (7.3).[18] The C-H insertion selectivity of 2, however, might be leveled by steric effects originating at the encumbered carbenic center; steric hindrance would selectively disfavor *tert.* C-H insertion.

Adamantanylidene is surprisingly selective in olefinic cyclopropanation. Competition experiments[19] with isobutene, *cis*-butene, and *trans*-butene afforded relative reactivities of 1.00, 0.68, and 0.18, respectively, for additions of 2 at 25°C. These limited data are quite comparable to the analogous relative reactivities of CCl_2 at 25°C (1.00, 0.27, 0.18).[20] CCl_2 is a reasonably discriminating carbene, for which the carbene selectivity index, *m*, is 1.00.[21] Therefore, 2



4; $R_1 = R_2 = R_3 = Me$
5; $R_1 = Me$, $R_2 = R_3 = H$
6; $R_1 = R_2 = H$, $R_3 = Me$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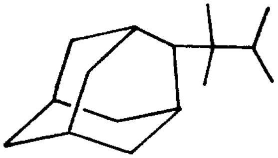
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appears to be more selective toward simple alkenes than expected, based upon extrapolation from the prototypal dialkylcarbene, Me_2C, for which we can *calculate*[21] $m \sim 0.2$. We caution, however, that the influence of differential steric selectivity on the olefinic discrimination of 2 is not yet known.

Photolyses of 1 in styrene, methyl acrylate, or acrylonitrile gave cyclopropanes 3e-3g in good yields (90%, 73%, 80%, respectively); neither adamantanone azine nor adamantanone were formed. We suggest that these reactions principally occur by photolytic reversion[22] of 1 to diazoadamantane, 1,3-dipolar addition of the diazoalkane to the electron deficient alkenes, and photolytic or thermal extrusion of nitrogen from the resultant pyrazolines, affording the final products.[23] Note, in support of these ideas, that the photolytic decompositions of alkyl- and aryl-substituted diazirines proceed, at least in part, via initial reversion to the linear diazo isomers;[22] this is also the case for 1.[13] We observed that photolysis of 1 at low temperature in pentane gave a reddish solution which was very rapidly bleached upon the addition of methyl acrylate at -78°C. Photolysis of 1 in mixtures of methyl acrylate and *cis*-butene gave mainly 3f, with apparent $k_{acrylate}/k_{cis\text{-}butene}$ values of ~36. Rather than attributing this to nucleophilic or ambiphilic selectivity[21] of carbene 2 (entirely unexpected, based upon its structure[21]), we suggest preferential dipolar addition of photogenerated diazoadamantane to methyl acrylate (ultimately affording 3f), in competition with a minor photogeneration of carbene 2, which adds mainly to *cis*-butene affording 3c. It should be noted that these "formal additions" of adamantanylidene to electron deficient alkenes proceed in synthetically acceptable yields.

Adamantanylidene thus appears to be moderately selective in C-H insertion and C=C addition reactions. Its further chemistry remains to be more fully defined, particularly the detection of its presumed triplet ground state.[24]

Acknowledgments. We are grateful to the National Science Foundation for financial support, and to Professor J. R. Knowles for a helpful discussion.

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