Crystal Data. $C_{13}H_{12}O_4$: $M_r = 232.2$, $a = 11.472$ (2) Å, $b = 7.635$ (2) Å, $c = 12.260$ (1) Å, $\beta = 96.72$ (1), $V = 1066.4$ (4) Å^3, $Z = 4$, $d_c = 1.45$ g cm^{-3}, $\mu = 9.09$ cm^{-1}.

Of the 1773 independent reflections collected, 961 had intensities greater than $3\sigma(I)$. Phases were calculated for the 191 $|E|$ values greater than 1.20 and the phase set with highest combined figure of merit yielded an E map that revealed the positions of all nonhydrogen atoms. After anisotropic refinement, all hydrogen atoms were located in a difference map. An isotropic extinction correction[22] introduced in the last cycles of refinement refined to a value of 11.8 (2) × 10^{-3} and yielded a final R factor of 0.035.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the National Institutes of Health for support of this work.

Registry No. 1, 17397-31-8; **2**, 19479-86-8; **3**, 73711-63-4; **4**, 73654-74-7; **5**, 17397-36-3; **6**, 81495-66-1; **7**, 81423-95-2; **8**, 81446-05-1; **9**, 81423-96-3; **10**, 81423-97-4; **12**, 81423-98-5; **13**, 81423-99-6; **14**, 81424-00-2; **15**, 81446-06-2; **16**, 81424-01-3.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, and observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

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o-Carboranylcarbene and *m*-Carboranylcarbene[1,2]

Sarangan L. Chari, Sheau-Hwa Chiang, and Maitland Jones, Jr.*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received July 30, 1981

Abstract: Addition of *o*- and *m*-carboranylcarbene to olefins takes place in a largely stereospecific fashion. In the addition to cis olefins, it is the anti isomer that predominates. Insertion into carbon–hydrogen bonds occurs with a secondary/primary selectivity ratio of 3.0. (Methyl-*o*-carboranyl)carbene behaves like tolylcarbene in intramolecular reactions. It yields vinyl-*o*-carborane and the carborane analogue of benzocyclobutene. (Methyl-*m*-carboranyl)carbene does not give vinyl-*m*-carborane.

If one were set the task of choosing the archetypal carbene, one might well settle on phenylcarbene.[3] Not only are the properties of both the addition and insertion reactions well worked out but also it is possible to generate the carbene from several sources. This is important because comparisons of properties of the intermediate formed from several sources allow identification of the common reaction species as the *carbene*. Thus in this case, but not all others, reactive nitrogen-containing intermediates derived from phenyldiazomethane can be eliminated.[4] We wondered if the stability conferred by a phenyl group upon an adjacent divalent carbon would be duplicated by a carborane. Would the effect of "two-dimensional" aromaticity be resembled by those of the "three-dimensional" or "super aromaticity" of the carboranes? In considering the possibilities we must examine steric, inductive, and resonance effects.[5]

The term "superaromatic" has been justified by a variety of MO treatments.[5,6] A system of 13 bonding MO's is nicely filled by the 26 electrons (6 from the two carbons, 20 from the 10 borons) involved in framework bonding. The predicted stability finds support in the ease of substitution reactions[5,7] and of course in the renowned stability of the icosahedral frame which routinely survives 400 °C, suffering at higher temperatures only rearrangement from the ortho isomer to the meta (ca. 500 °C, quantitative in a flowing system at 600 °C) followed by a less clean conversion to para (50% at >600 °C).[5,8] However, it is *not* clear that this thermodynamic stability is accompanied by stabilizing effects on attached positions, as clearly is the case in benzene and its derivatives. A study of arylcarboranes showed that although the two icosahedrons, and especially the ortho isomer, were highly electron withdrawing inductively, there was no substantial ground state "extension of electron delocalization by interaction with the aryl group".[9] Similarly, there is no strong case to be made that the analogue of naphthalene, in which one benzene ring is replaced by a carborane,[10] is more than a diene appended to the icosahedron. Only the NMR spectrum provides tenuous evidence of aromatic behavior. Even here the chemical shift of the diene protons is only 0.2–0.3 ppm downfield from that expected of a diene.[11] Of direct impact on our projected work was the finding of Hutton and Roth of the Bell Laboratories group, along with one of us, that EPR spectra of *o*-carboranylcarbene and a C-methylated derivative showed little delocalization of π-spin density.[12]

On first thought it might be expected that there would be enormous steric differences between the flat, six-atom frame benzene ring and the 12-atom frame, three-dimensional icosahedral carboranes. Not so. The 2.8-Å para C–C bond distance in benzene is increased by only a few tenths of 1 Å in the various "para" distances in *o*-, *m*-, and *p*-carboranes.[6] The size difference is not so great as one might imagine. Carboranes are the size of slightly elongated, rotating benzene rings. One possible indication that size differences will be of minor import is the observation that in the interaction of *o*-carboranyl alanine with chymotrypsin, the carboranyl group could bind with the "phenyl recognition site".[13]

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* It gives us great pleasure to dedicate this paper to Professor William von Eggers Doering on the occasion of his 65th birthday.

(1) *o*-Carborane and *m*-carborane are 1,2-dicarba-*closo*-dodecaborane (12) and 1,7-dicarba-*closo*-dodecaborane (12), respectively.

(2) A portion of this work was previously communicated: Chari, S.; Agopian, G. K.; Jones, M., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6125. Other portions come from the Ph.D. Thesis of S.L.C., Princeton University, 1981.

(3) For a summary see: Jones, M., Jr., Moss R. A., Eds. "Carbenes"; Wiley: New York, 1973; Vol. 1, pp 64-73.

(4) For cases in which excited diazo compounds may play a role see: Moss, R. A.; Jones, M., Jr. In "Reactive Intermediates"; Wiley: New York, 1981; Vol. 2, Chapter 3.

(5) (a) Grimes, R. N. "Carboranes", Academic Press: New York, 1970. (b) Onak, T. "Organoborane Chemistry"; Academic Press: New York, 1975. (c) Beall, H. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 9.

(6) Bohn, R. K.; Bohn, M. D. *Inorg. Chem.* **1971**, *10*, 350.

(7) For examples see: Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 1471, 1478, 1483 (*o*-carborane). Stanko, V. I.; Klimova, A. I.; Titova, N. S. *Zh. Obshch. Khim.* **1968**, *38*, 2817 (*m*-carborane).

(8) Papetti, S.; Obenland, C.; Heying, T. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 334.

(9) Hawthorne, M. F.; Berry, T. E.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 4746.

(10) Matteson, D. S.; Hota, N. K. *J. Am. Chem. Soc.* **1971**, *93*, 2893.

(11) Cooper, M. A.; Manatt, S. L. *J. Am. Chem. Soc.* **1969**, *91*, 6325; **1970**, *92*, 1605.

(12) Hutton, R. S.; Roth, H. D.; Chari, S. *J. Phys. Chem.* **1981**, *85*, 753.

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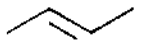
Table I. Typical Stereochemistry of Cyclopropanes Formed by "Aryl" Carbene Additions[a]

carbene	olefin	trans cyclopropane	cis/syn cyclopropane	cis/syn cyclopropane
phenylcarbene[15,16]		97	3 (0.5–1)	
		2.5 (3–5)	51.1	46.4
o-caroboranyl-carbene		100	<1	
		<1	5	95
m-carboranyl-carbene		94	0	6
		6	27	67

[a] Normalized to 100%; insertion products ignored.

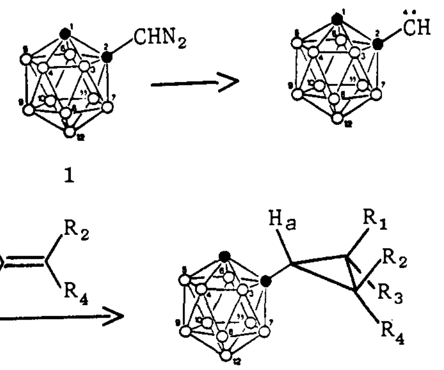
Intermolecular Chemistry. Phenylcarbene is a ground-state triplet[14] and yet reacts stereospecifically with olefins.[3] Attempts to generate directly the lower energy triplet lead to the same nearly stereospecific addition. The addition reaction is evidently going through the less stable but far more reactive singlet state which is in equilibrium with the more stable, but less reactive, triplet. Phenylcarbene generated from photolysis of stilbene oxide behaves indistinguishably[3,15] from that formed by irradiation of phenyldiazomethane. Thus the properties reported must be those of a common carbene intermediate, and there can be no serious intervention of precursor-derived reactions.

Although the addition reactions of phenylcarbenes are almost stereospecific, there are of course two possible cis adducts to *cis*-2-butene. Surprisingly, it is the syn epimer that is favored, albeit but slightly (syn/anti = 1.1).[16] Although certainly surprisingly on steric grounds, there have been both classical electrostatic[16] and MO-based explanations,[17,18] and similar phenomena have been observed in the electrophilic addition of singlet oxygen to olefins.[19] Several points of comparison are possible between addition reactions of phenylcarbene and carboranylcarbenes.

o-Carboranylcarboxaldehyde tosylhydrazone was synthesized from the commerically available *o*-vinylcarborane by careful ozonolysis to give the aldehyde and unexceptional formation of the tosylhydrazone. Treatment with sodium hydride followed by pyrolysis at 70–90 °C led to the diazo compound **1** in poor yield. Reactions were carried out by dissolving **1** in a large excess of substrate, degassing by freeze–thaw procedures, and irradiating sealed Pyrex tubes with a 450-W Hanovia medium-pressure mercury arc for 4–5 h. Products were collected by gas chromatography of the concentrated reaction mixtures.

Irradiation in *trans*-2-butene led to a single cyclopropane, **2a**, as was the case for the analogous reaction of phenylcarbene.[16] The two different methyl groups appear as doublets ($J \simeq 6$ Hz) at δ 1.26 and 1.03. Proton H_a is coupled to both R_2 and R_3. No evidence for either possible cis isomer was found. The IR spectrum of **2a** showed, as did the spectra of all the cyclopropanes formed from irradiation of **1**, the characteristic B-H stretching vibration at 2600 cm^{-1}. The spectrum was very similar to that reported for cyclopropyl-*o*-carborane synthesized from decarborane and cyclopropylacetylene by Nefedov's group.[20]

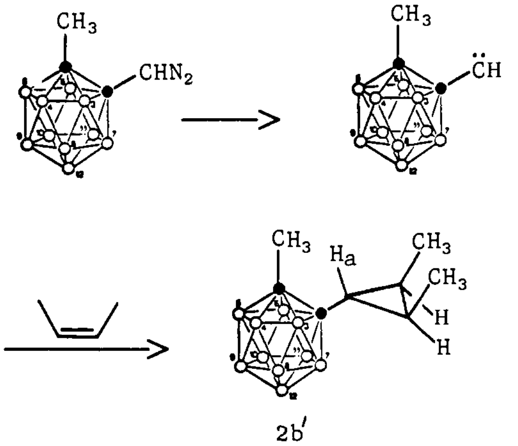
Addition to *cis*-2-butene led to a ca. 20:1 mixture of two cyclopropanes, **2b** and **2c**, both of which were different from **2a**. One's expectation naturally is that **2b** and **2c** must share the two possible structures, cis/syn and cis/anti. The major problem is to tell which is which. The identification of **2a** as trans is secure: only the trans compound can show two different methyl signals. A similar problem was found in the analysis of the cis adducts formed from phenylcarbene, and in this case degradation studies left no doubt that the cis/syn product was favored by a very small amount.[16,21] Regardless of how the argument is couched, preferential formation of the syn isomer requires either dispersion of charge into the benzene ring and/or MO extension over the aromatic system. In either event there must be significant interaction between the aromatic nucleus and the carbene in the transition state for addition. One might well anticipate that in carboranylcarbene addition the increased steric effects would compete more favorably against the electronic effects that favor syn addition. This is the case. The major cis cyclopropane found from *o*-carboranylcarbene and *cis*-2-butene is the anti compound, not the conventional syn. Although at 60 or 90 MHz the ^{1}H NMR spectrum is uninformative, at 400 MHz all becomes clear.[22] In particular, it becomes easy to measure the coupling constant between H_a and the other two protons on the three-membered ring. In the minor product, **2c**, $J_{H_a\text{-}H}$ is 9.0 Hz. In the major product, **2b**, this coupling constant is much smaller. In **2b** it is less well resolved than in **2c**, but still is clearly about half the value for **2c**. In **2b′** H_a is better resolved and the crucial coupling constant can be easily determined to be 4.7 Hz. Thus the minor product clearly incorporates a typical cis coupling constant of ca. 9 Hz whereas the major product has a typical trans coupling constant of ca. 5 Hz.[23] Addition of *o*-carboranylcarbene is stereospecifically cis and proceeds in largely anti fashion.



1

2a–g

a, $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$; b, $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$; c, $R_3 = R_4 = CH_3$, $R_1 = R_2 = H$; d, $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$; e, $R_1 = R_3 = R_4 = CH_3$, $R_2 = H$; f, $R_1 = R_2 = R_3 = CH_3$, $R_4 = H$; g, $R_1 = R_2 = R_3 = R_4 = CH_3$



2b′

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(13) Fischli, W.; Leukart, O.; Schwyzer, R. *Helv. Chim. Acta* **1977**, *60*, 959.

(14) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, 84, 4990.

(15) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153.

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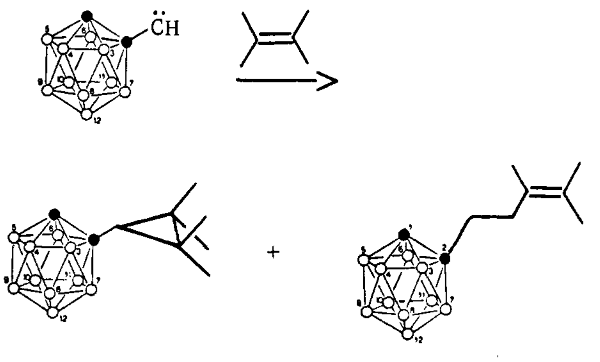
(21) Gutsche, C. D.; Bachman, G. L.; Coffey, R. S. *Tetrahedron* **1962**, *18*, 617.

(22) The 400-MHz ^{1}H NMR spectra were run by the University of South Carolina Magnetic Resonance Laboratory.

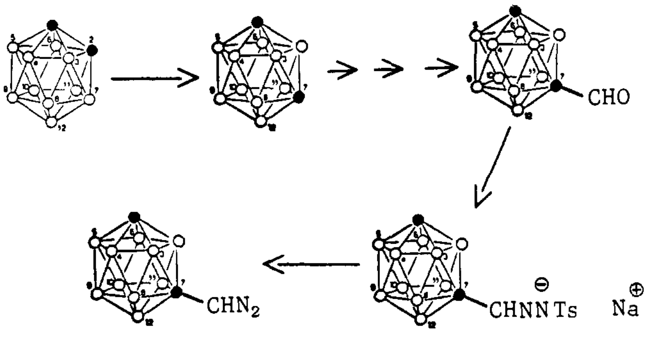
(23) Becker, E. D. "High Resolution NMR", 2nd ed.; Academic Press: New York, 1980.

Addition of *o*-carboranylcarbene also proceeds well with other olefins. Isobutylene, 2-methyl-2-butene and 2,3-dimethyl-2-butene form adducts **2d**, **2e** and **2f**, and **2g**, respectively. Cyclopropane **2f** was favored over **2e** by a factor of ca. 3. The tetrasubstituted olefin yields **2g** accompanied by 15% of the product of insertion into the allylic carbon–hydrogen bond. Phenylcarbene is said to produce "a few percent"[16] of insertion.



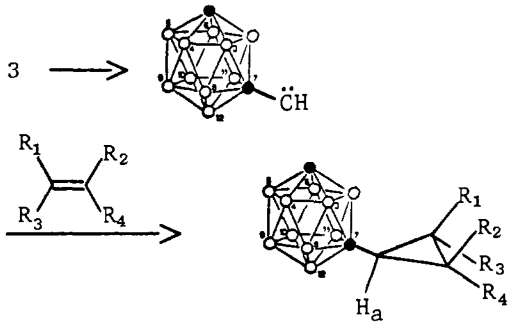
2g

The reactions of *m*-carboranylcarbene are qualitatively similar.



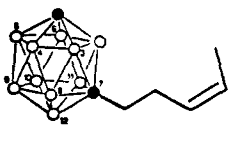
3

o-Carborane was quantitatively rearranged to *m*-carborane in a flowing system at 640 °C. Conversion to the aldehyde and tosylhydrazone salt was routine. Pyrolysis of the salt at 70 °C led to *m*-carboranyldiazomethane (**3**) in modest yield. Irradiation in *trans*-2-butene led to three products in 34% combined yield.[24] The major one (73%) was the trans cyclopropane **4a** and was identified by the appearance of two doublet signals for the methyl groups. Substantial amounts (19%) of an insertion product **5** and 5% of a second cyclopropane, **4b**, were also found. Addition to *cis*-2-butene also led to several products in 26% combined yield.[24] Two cis cyclopropanes, **4b** and **4c**, were found in 58 and 23% yields, respectively. The trans cyclopropane, **4a**, was present in 5% and there was 14% of the insertion product, **6**. The two cis cyclopropanes, **4b** and **4c**, were distinguished by an examination of the 400-MHz ^{1}H NMR spectra.[22] The major product, **4b**, showed a coupling between H$_a$ and the two other cyclopropane protons of 4.8 Hz and the minor product, **4c**, a coupling of 9.6 Hz. Thus **4b** is the cis/anti adduct and **4c** the cis/syn adduct.

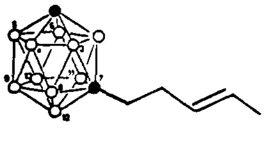


4a–c

a, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$; b, $R_3 = R_4 = CH_3$; $R_1 = R_2 = H$; c, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$



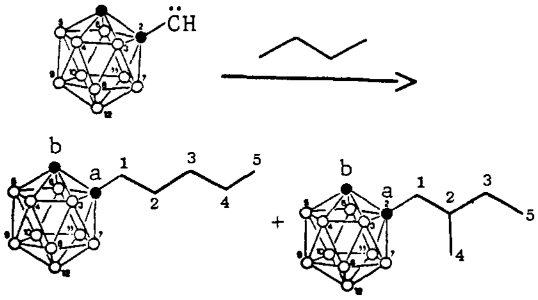
6



5

Therefore, addition of both *o*-carboranylcarbene and *m*-carboranylcarbene is largely stereospecific, as it is with phenylcarbene (see Table I). The only significant difference is the change in the addition to *cis*-2-butene from a favoring of syn adduct by phenylcarbene to a predominance of the anti adducts in the reactions of the two carboranylcarbenes. We have touched upon possible reasons for this earlier, but it is worth pointing out that very small energy differences are involved. The ratio for phenylcarbene represents a trivial energy difference, and *o*- and *m*-carboranylcarbene favor the anti compounds by ca. 1.7 and 0.5 kcal/mol, respectively. A small increase in steric demand, coupled with a decrease in electronic favoring of syn addition, easily suffices to rationalize these small energy differences.

Insertion Reactions. Carbenes reacting in their singlet states show varying preferences for more highly substituted carbon-hydrogen bonds over less substituted (tertiary > secondary > primary) depending upon the degree of internal stabilization of these electrophilic species.[3] Griffin and his co-workers[15] found that phenylcarbene generated by photolysis of a variety of oxirane and cyclopropane precursors favored the secondary over primary positions in *n*-pentane by an average factor of 8.4. Phenylcarbene from photolysis of phenyldiazomethane gave ratios of 8.2–8.6. The analytical problems encountered by Griffin[15] provoked us to use the more simple *n*-butane as a substrate for a determination of the selectivity in the insertion reaction of *o*-carboranylcarbene. Two products (**7** and **8**) were found in a 1:2 ratio on photolysis of a solution of **1** in *n*-butane. The structures of the two products were established by high-resolution mass spectra and ^{13}C NMR spectra. The 90-MHz ^{1}H NMR spectra were uninformative, but the off-resonance ^{13}C spectra allowed us to see the coupling patterns of the ^{13}C with adjacent protons. These couplings, combined with the knowledge that the ^{13}C chemical shifts of the alkyl carbons move upfield as the carbons move progressively further from the cage carbon,[25] allow an unequivocal assignment (Table II). Thus *o*-carboranylcarbene prefers, on a per bond basis, secondary over primary carbon-hydrogen bonds by a factor of 3, a number slightly different from the factor of ca. 8 shown by phenylcarbene. Again an increased steric demand and decreased electronic interaction in the transition state is suggested.



7 8

Intramolecular Chemistry. D. S. Matteson once likened carborane chemistry to the music of Vivaldi,[26] "straightforward to

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[24] Yields are based on the amount of tosylhydrazone used. They represent in fact the combined yields of three steps: tosylhydrazone salt formation, pyrolytic production of the diazo compound, and the addition reaction.

[25] Wrackmeyer, B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227.

[26] Matteson, D. S. *J. Organomet. Chem.* **1978**, *17*, 147.

Scheme I

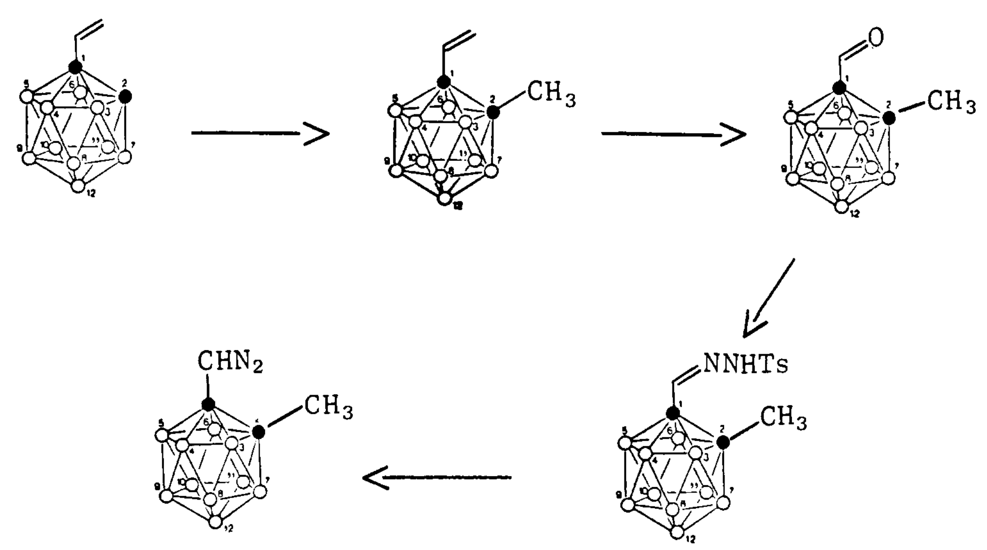
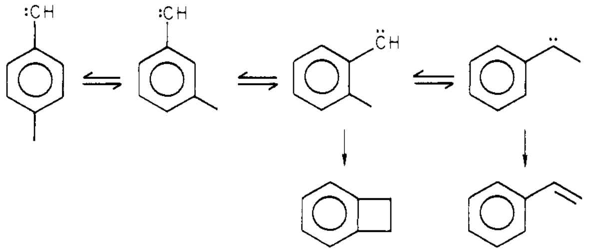
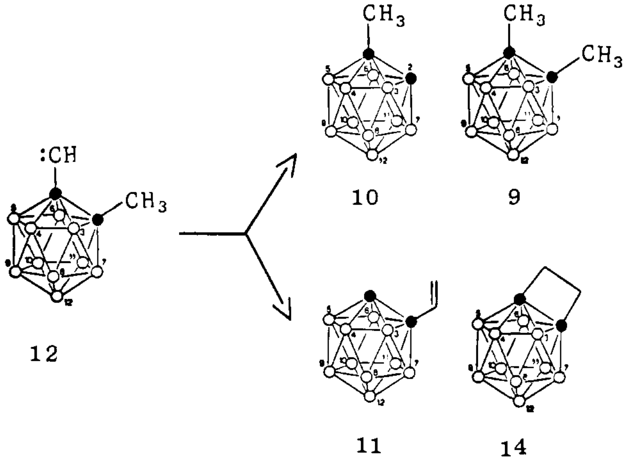


Table II. ^{13}C NMR Spectra of 7 and 8

compd	δ	multiplicity	assignmt
7	71.66	singlet	carborane C_a
	61.31	doublet	carborane C_b
	37.91	triplet	C_1
	31.08	triplet	C_2
	28.86	triplet	C_3
	22.31	triplet	C_4
	13.95	quartet	C_5
8	75.56	singlet	carborane C_a
	62.56	doublet	carborane C_b
	44.79	triplet	C_1
	34.82	doublet	C_2
	29.78	triplet	C_3
	19.98	quartet	C_4
	11.04	quartet	C_5

perform, an endless supply of variations on a theme, pleasant enough, but more interesting to the performers than the spectators". We think the work described above is more than routine, but it does represent mainstream chemistry, at least in that no new reactions or properties of carbenes are reported and no spectacular effects of the borons appear. In this short section we describe the beginnings of our work on nontraditional carborane chemistry in which reactions occur that are difficult to describe completely in mechanistic terms. This section is more Webern than Vivaldi.[27] Although most intermolecular reactions of carbenes have their intramolecular counterparts (addition, insertions, etc.), a few such as the simple phenylcarbene rearrangement do not.[28] In this reaction a benzene ring acts as a conduit, through which a divalent carbon passes to another position.[29] We have already seen that the "super aromatic" *o*- and *m*-carboranylcarbenes are well-behaved species, rather like phenylcarbene in their intermolecular chemistry. In order to probe the extent of similarity between *o*- and *m*-carboranylcarbenes and phenylcarbene, we decided to see if we could find a reaction analogous to the well-known rearrangements of the tolylcarbenes.[28,30] In this system rearrangement takes place until *o*-tolylcarbene or methylphenylcarbene is reached and intramolecular insertion takes place to give benzocyclobutene and styrene. In order to follow the tolylcarbene system, we synthesized 1-methyl-*o*-carboranyldiazomethane from vinyl-*o*-carborane as shown in Scheme I. Gas-phase pyrolysis by various methods (see Experimental Section) led to the same set of four products, although the most efficient method used in situ generation of the diazo compound by gentle heating of the tosylhydrazone salt under 10^{-3} torr vacuum. Analysis of the products showed the known 1,2-dimethyl-*o*-carborane (**9**) and 1-methyl-*o*-carborane (**10**).





Compound **9** is the apparent product of hydrogen abstraction by the carbene. This is an uncommon but precedented reaction.[31] The monomethyl compound **10** is probably the product of base-induced cleavage of the side chain.

The third compound, 1-vinyl-*o*-carborane (**11**) was identified by comparison with authentic material. On the surface the isolation of **11** provides strong evidence for the rearrangement of 1-methyl-*o*-carboranylcarbene (**12**) to the new carbene **13**, much as *o*-tolylcarbene rearranges to methylphenylcarbene. But a

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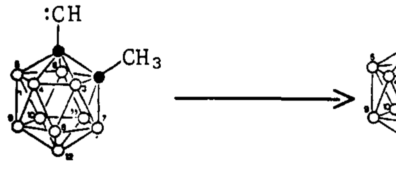
(27) This is a presumptuous comparison at best. We generally feel more like a troop of wandering kazoo players who happen occasionally upon a melody than like accomplished musicians.

(28) (a) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. (b) Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Lehr, R.; Marchand, A., Eds.; Academic Press: New York, 1977; Vol. 1, p 109. (c) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173.

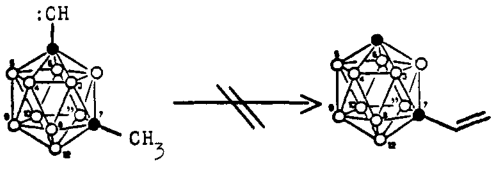
(29) Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1978**, 5193.

(30) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739. This rearrangement was suggested earlier: Vander Stouw, G. G. Ph.D. Dissertation, Ohio State University, 1965.

(31) The generation of phenylcarbene in the gas phase gives small amounts of toluene: Pacala, L. L.; Font, J.; Hollowood, F., unpublished results.



12 13



15

problem intrudes. The fourth product is **14**, the carborane analogue of benzocyclobutene. This compound is not known, but NMR spectroscopy readily provided the structure. The ^{1}H NMR spectrum shows, in addition to aromatic signals, a single peak at δ 2.9. The ^{13}C NMR spectrum shows two signals at 36.39 and 79.68 ppm. The latter can be assigned to the cage carbons, as it remains unchanged on partial undecoupling. The other peak elaborates to a triplet and clearly represents the methylene carbon. Compound **14** is the first example of a carborane fused to a carbocyclic four-membered ring. The related five-membered ring is known,[32] and several six-membered rings have been reported,[5] but **14** now represents the lower limit for carbocyclic rings.[33] Presumably **14** is produced by direct insertion of the divalent carbon into the proximate methyl group. Could **14** be the source of **11**? At high temperature benzocyclobutene does yield styrene,[34] and the properties of **14** were certainly unknown. Even though **14** survives unchanged after heating at 350 °C for 24 h, the question remains unsettled. If **14** is formed by an insertion reaction of carbene **12**, the reaction is surely exothermic. In the gas phase the chances for collisional deactivation of the resulting "hot" **14** are limited, and it seemed to us that the simple control experiment described above was inadequate. Accordingly, we undertook a labeling experiment, taking advantage of the equivalence of the two "cyclobutenyl" carbons in **14** (Scheme II).

We prepared ^{13}C methyl labeled methyl-*o*-carboranylcarbene. If **14** is an intermediate, the vinyl-*o*-carborane produced must be labeled in both olefinic positions. Phenylcarbene rearrangement, on the other hand, must give only terminally labeled product. The product from labeled carbene showed a single enhanced peak at δ 122.8 in the ^{13}C NMR spectrum. The unlabeled compound has been reported to have two olefinic carbons at δ 122.4 and 132.7.[35] We confirmed the assignment of the 122.8-ppm peak to the terminal carbon by an off-resonance experiment in which this signal appears as a triplet. The location of the label exclusively in the terminal position eliminates **14** as a source of the vinyl-*o*-carborane and points directly to a process akin to the phenylcarbene rearrangement. As debate continues as to the nature of the intermediates in even the simple phenylcarbene rearrangement,[28] it would be presumptuous to speculate too much in the absence of further experiments. However, icosahedral carboranes are known to undergo cage expansion to give various 13-vertex metallocarboranes.[5] A purely speculative mechanism posits a cage expansion induced by the divalent carbon to such a 13 vertex, probably nido species. The corresponding closo species would have to be isoelectronic with $B_{13}H_{13}^{2-}$ or $C_3B_{10}H_{13}^{+}$. That is, the intermediate would need to be protonated in order to assume a closo form. As the cage could be reformed in two ways, rearrangement becomes possible. We have not yet been able to trap intermediates, however.

In the formation of vinyl-*o*-carborane, the 10 boron atoms *may* act merely as a frame, holding the reactive carbon-based part of the molecule together. It was of interest to see whether the analogous meta species in which a ring of borons must be traversed by the rearranging carbon could also undergo the reaction. The answer appears to be "no". Generation of carbene **15** and examination of the products by GC–mass spectroscopy revealed no peaks of the mass (m/e 172) appropriate for vinyl-*m*-carborane. Within the limits set upon all negative results, vinyl-*m*-carborane is not found and, therefore, rearrangement is not taking place.

Experimental Section

General Remarks. Melting points were determined by using a Thomas Hoover Unimelt apparatus and are uncorrected.

Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA.

Routine nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer (60 MHz), a Perkin-Elmer R-32 spectrometer (90 MHz) (continuous-wave operation), a Varian XL-100 spectrometer (^{1}H 100.083 MHz, ^{13}C 25.196 MHz) or JEOLCO-JEOL FX 90 Q spectrometer (^{1}H NMR 89.55 MHz, ^{13}C 22.50 MHz) (Fourier transform mode).[22]

Infrared spectra were recorded on a Perkin-Elmer 283 IR spectrophotometer.

Analytical gas chromatography was performed on a Varian 1400 gas chromatograph (flame ionization detector) with nitrogen as carrier gas, using $^1/_8$-in. stainless-steel columns. Preparative gas chromatography was performed on a Varian A-90A gas chromatograph (thermal conductivity detector) with helium as carrier gas, using $^1/_4$-in. aluminum columns.

Mass spectra were obtained on an AEI MS-9 mass spectrometer (electron impact). GC/MS runs were conducted on a Du Pont 21-490 GC-MS interfaced to a Varian 1400 gas chromatograph (FID-EI).

In general, reaction were conducted under an inert atmosphere of nitrogen or argon using a manifold. All solvents were purified and dried by using standard procedures. Normal syringe and airless techniques were employed.

1-Formyl-*o*-carborane. Vinyl-*o*-carborane (1.72 g, 0.01 mol) was dissolved in dry methanol (40 mL) in a three-necked flask equipped with an inlet tube and a Dry Ice condenser. Ozonized oxygen (0.5 L/min), generated by using a Welsbach ozonizer operated at an inlet pressure 7–8 psi and 100 W, was bubbled in while the temperature was maintained between −50 and −40 °C. The reaction was monitored by TLC (silica gel, hexane) to completion (40 min). The reaction mixture was purged with nitrogen and treated with dimethyl sulfide (4-mL excess), added all at once. It was allowed to warm up to room temperature and stand for 4 h. The solvent was stripped, and the residue was extracted with ether, washed with brine, and dried over sodium sulfate. Evaporation of the ether and sublimation yielded 1-formyl-*o*-carborane (1.32 g, 71%): mp 207–209 °C [lit.[36] mp 208–209 °C]; ^{1}H NMR ($CDCl_3$) δ 9.25 (s, formyl H), 4.05 (br s, carborane H); IR ($CHCl_3$) 3060, 2580, 1745 cm^{-1}.

1-Formyl-*o*-carborane Tosylhydrazone. To a solution of 1-formyl-*o*-carborane (0.87 g, 0.005 mol) in methanol (25 mL) was added *p*-toluenesulfonyl hydrazide (0.95 g, 0.005 mol). Two drops of concentrated hydrochloric acid was added as catalyst and the mixture refluxed for 5 h. Hot distilled water was added to the reaction mixture until turbidity appeared. The tosylhydrazone crystallized on cooling (1.05 g, 60%), and was recrystallized from methanol to yield an analytical sample: mp 195–196 °C; ^{1}H NMR (Me_2SO-d_6) δ 12.1 (s, N-H), 7.85–7.4 (q, aromatic H's), 6.25 (br s, carborane H), 4.8 (s, methine), 2.4 (s, tolyl methyl); IR (Nujol) 3220, 3060, 2580, 1600 cm^{-1}. Anal. Calcd for $B_{10}C_{10}H_{20}N_2O_2S$: C, 35.09; H, 5.85. Found: C, 34.29; H, 6.06.

1-Diazomethyl-*o*-carborane. A solution of 1-formyl-*o*-carborane tosylhydrazone (1.0 g, 0.003 mol) in dry THF (25 mL) was cooled to −78 °C. Sodium hydride, 50% dispersion in oil (0.14 g, 0.003 mol), was washed well with dry pentane, dried and slurried with dry THF, and added by syringe to the tosylhydrazone solution. The temperature was slowly raised until hydrogen evolution was noticed and held until it ended. The THF was removed, and the resulting gummy mass was triturated with dry pentane to remove the residual THF, and the sodium salt of the tosylhydrazone so obtained was placed in a vacuum dessicator and pumped dry overnight. The sodium salt thus obtained was pyrolyzed in a flask which was attached to a series of bulbs surrounded by Dry Ice

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[32] Zakharkin, L. I.; Grebinnekov, A. V.; Kazantsev, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2077.

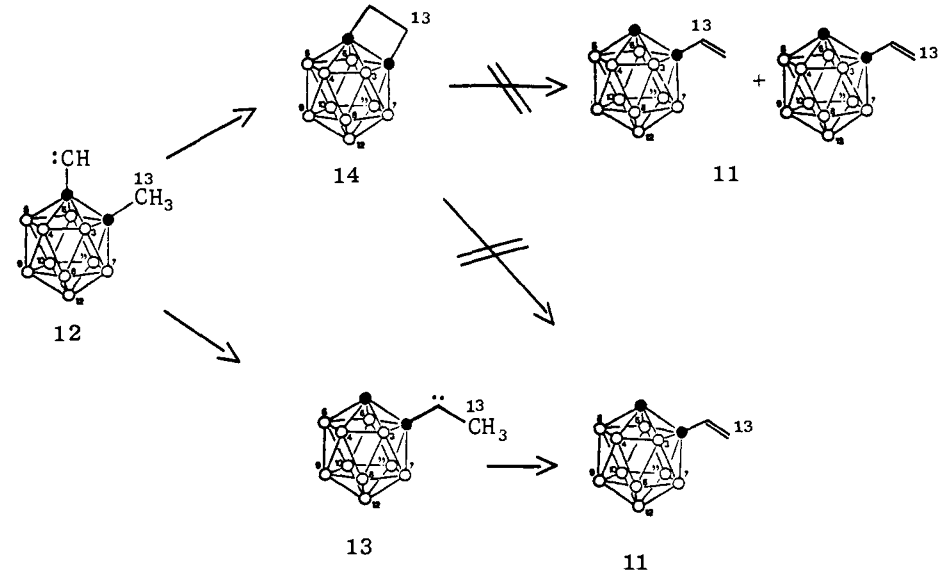
[33] For reports of three-membered rings containing metals, see: Zakharkin, L. I.; Kovredov, A. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2619; Sayler, A. A.; Beall, H.; Sieckhaus, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 5790.

[34] Baron, W. J.; DeCamp, M. R. *Tetrahedron Lett.* **1973**, 4225.

[35] Todd, L. J.; Seidle, A. R.; Bodner, G. M.; Kahl, S. B.; Hickey, J. P. *J. Magn. Reson.* **1976**, *23*, 301.

[36] Stanko, V. I.; Brattsev, V. A.; Alperovich, N. E.; Titova, N. S. *Zh. Obshch. Khim.* **1968**, *38*, 1056.

Scheme II



and connected to a vacuum and inert gas source by a valve. The flask was placed in a Kugelrohr oven and evacuated to 0.1 torr, and the oven temperature was raised slowly to 70–90 °C, when decomposition occurred to yield the yellow diazo compound which condensed in the bulbs (IR 2580, 2080 cm^{-1}). It was used in reactions immediately.

General Procedure for Intermolecular Reactions with 1-Diazomethyl-*o*-carborane. The still-frozen diazo compound was washed into a quartz tube, equipped with a T-joint closed by a high-vacuum Teflon stopcock, by liquid reactants or by condensation of gaseous reactants (butane, butenes). The solution which contained a large excess of the reactant was degassed by the freeze-thaw method and the stopcock closed. The quartz tube was now irradiated by a 450-W medium-pressure Hanovia lamp through Pyrex in a water-cooled bath. The diazo compound was completely decomposed in 4–5 h as seen by the discharge of the yellow color. The tube was cooled and opened, and the excess reactant removed. The crude product was chromatographed and collected by using either a 6-ft 10% OV-17/Gas-chrom Q 60-80 or a 6-ft 10% SE-30/Gas-chrom Q 60-80 column.

anti-1,2-*cis*-Dimethyl-3-*o*-carboranylcyclopropane. This was isolated as the major product (~95%) from the photolysis of 1-diazomethyl-*o*-carborane in *cis*-2-butene by preparative GC: precise mass calculated for $C_7B_{10}H_{20}$ 214.2496, found 214.2502; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (br s, 1, carborane H), 2.7–1.4 (m, B-H), 0.99 (br s, 8, methyl and cyclopropyl H), 0.82 (t, 1, H$_a$); IR (CCl_4) 3080, 3020, 2600 cm^{-1}.

***syn*-1,2-*cis*-Dimethyl-3-*o*-carboranylcyclopropane.** This was isolated as the minor product (~5%) from the photolysis of 1-diazomethyl-*o*-carborane in *cis*-2-butene by preparative GC: precise mass calculated for $C_7B_{10}H_{20}$ 214.2496, found 214.2505; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (br s, 1, carborane H), 1.7–2.9 (m, B-H), 1.36 (t, 1, J = 9.0 Hz, H$_a$), 1.47 (br s, 8, methyl and cyclopropyl H); ^{13}C NMR ($CDCl_3$) δ 25.86, 17.08, 7.5; IR ($CDCl_3$) 3080, 3000, 2580 cm^{-1}.

***trans*-1,2-Dimethyl-3-*o*-carboranylcyclopropane.** This was isolated from the photolysis of 1-diazomethyl-*o*-carborane in *trans*-2-butene by preparative GC: precise mass calculated for $C_7B_{10}H_{20}$ 214.2496, found 214.2502; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (br s, 1, carborane-H), 1.4–2.9 (m, B-H), 1.26 (d, 3, J = 6.6 Hz, methyl), 1.11 (m, 1, cyclopropyl), 1.03 (d, 3, J = 5.8 Hz, methyl), 0.81 (m, 1, cyclopropyl), 0.69 (m, 1, cyclopropyl H$_a$); IR (neat) 3060, 3000, 2580 cm^{-1}.

***anti*-1,2-*cis*-Dimethyl-3-(1-methyl-*o*-carboranyl)cyclopropane.** This was isolated from the photolysis of 1-diazomethyl-2-methyl-*o*-carborane in *cis*-2-butene by preparative GC: precise mass calculated for $C_8B_{10}H_{22}$ 228.2659; found 228.2652; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.4–3.0 (m, B-H), 2.02 (s, 3, carborane methyl), 1.11 (m, 2, cyclopropyl), 1.44 (d, 6, J = 5.2 Hz, methyl), 0.70 (t, 1, J = 4.6 Hz, H$_a$); IR (CCl_4) 3030, 2590 cm^{-1}.

1,1-Dimethyl-2-*o*-carboranylcyclopropane. This was isolated from the photolysis of 1-diazomethyl-*o*-carborane in isobutylene by preparative GC: precise mass calculated for $C_7B_{10}H_{10}$ 214.2496, found 214.2504; ^{1}H NMR (benzene) δ 2.7 (br s, carborane H), 1.0 (s, methyl), 0.65 (s, methyl), 0.9–0.2 (m, cyclopropyl); IR (CCl_4) 3080, 3000, 2580 cm^{-1}.

1,1-Dimethyl-2-*trans*-methyl-3-*o*-carboranylcyclopropane. This was isolated as the major product (~75%) from the photolysis of 1-diazomethyl-*o*-carborane in trimethylethylene by preparative GC: precise mass calculated for $C_8B_{10}H_{22}$ 228.2652, found 228.2661; ^{1}H NMR (benzene) δ 2.75 (br s, carborane H), 1.0 (s, methyl), 0.65 (s, methyls), 0.8–0.3 (m, cyclopropyl).

1,1-Dimethyl-2-*cis*-methyl-3-*o*-carboranylcyclopropane. This was isolated as the minor product (~25%) from the photolysis of 1-diazomethyl-*o*-carborane in trimethylethylene by preparative GC: precise mass calculated for $C_8B_{10}H_{22}$ 228.2652, found 228.2659; ^{1}H NMR (benzene) δ 2.75 (br s, carborane H), 1.2–1.0 (3 s, methyls), 1.3–0.8 (m, cyclopropyl); ^{13}C NMR (acetone-d_6) δ 77.93, 66.34, 34.16, 30.20, 26.30, 23.87, 15.09, 8.86; IR (CCl_4) 3060, 3020, 2560 cm^{-1}.

1,1,2,2-Tetramethyl-3-*o*-carboranylcyclopropane. This was isolated as the major product (~85%) from the photolysis of 1-diazomethyl-*o*-carborane in tetramethylethylene by preparative GC: precise mass calculated for $C_9B_{10}H_{24}$ 242.2842, found 242.2832; ^{1}H NMR (benzene) δ 2.75 (br s, carborane H), 0.9 (s, methyl), 0.65 (s, methyl), 0.4 (br s, cyclopropyl); IR (CCl_4) 3080, 3030, 3000, 2580 cm^{-1}.

2,3-Dimethyl-5-*o*-carboranyl-2-pentene. This was isolated as the minor product (~15%) from the photolysis of 1-diazomethyl-*o*-carborane in tetramethylethylene by preparative GC: precise mass calculated for $C_9B_{10}H_{24}$ 242.2842, found 242.2839; ^{1}H NMR (benzene) δ 2.6 (br s, carborane H), 1.8 (br s), 1.5–1.2 (br d), 1.0–0.7 (m); ^{13}C NMR (acetone-d_6) δ 126.80, 125.50, 76.91, 63.31, 36.66, 35.03, 20.73, 20.08, 18.40; IR (neat) 3080, 2590 cm^{-1}.

1-(*n*-Pentyl)-*o*-carborane. This was isolated as the minor product (~33%) from the photolysis of 1-diazomethyl-*o*-carborane in *n*-butane by preparative GC: precise mass calculated for $C_7B_{10}H_{22}$ 216.2652, found 216.2656; ^{1}H NMR (benzene-d_6) δ 2.5 (br s, carborane H), 1.7–0.6 (m, aliphatic H); ^{13}C NMR (benzene-d_6) δ 71.60, 61.31, 37.91, 31.08, 28.86, 22.31, 13.96; IR (CCl_4) 3080, 2590 cm^{-1}.

1-(2-Methylbutyl)-*o*-carborane. This was isolated as the major product (~66%) in the photolysis of 1-diazomethyl-*o*-carborane in *n*-butane by preparative GC: precise mass calculated for $C_7B_{10}H_{22}$ 216.2652, found 216.2654; ^{1}H NMR (benzene-d_6) δ 2.8 (br s, carborane H), 2.0–0.8 (m, aliphatic H); ^{13}C NMR (benzene-d_6) δ 75.56, 62.56, 44.79, 34.82, 29.78, 19.98, 11.04; IR (CCl_4) 3080, 2590 cm^{-1}.

1-Methyl-2-vinyl-*o*-carborane. Vinyl-*o*-carborane (1.72 g, 0.01 mol) was dissolved in ether (25 mL). The solution was cooled to 0 °C, and *n*-butyllithium in hexane (1.6 M) (6.5 mL, 0.01 mol) added slowly. After the addition was complete, the mixture was allowed to stir for 2 h. A solution of methyl iodide (1.5 g, 0.01 mol) in ether (10 mL) was added slowly, and the resulting mixture was refluxed for 4 h and cooled. The reaction mixture was quenched with dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were washed with a saturated sodium bicarbonate solution and dried over sodium sulfate, and the solvent was removed. The residue was sublimed to yield the product as waxy crystals (1.41 g, 76%), mp 164–166 °C [lit.[37] mp 164–165 °C]; ^{1}H NMR ($CDCl_3$) δ 6.2–5.5 (m, 3, vinyl), 1.95 (s, 3, methyl); IR (CCl_4) 2580, 1635 cm^{-1}.

1-Methyl-2-formyl-*o*-carborane. 1-Methyl-2-vinyl-*o*-carborane (1.86 g, 0.01 mol) was dissolved in dry methanol (40 mL) and ozonized at −40 to −50 °C under previously described conditions. The progress of the

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(37) Zakharkin, L. I.; Kazantsev, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 2190.

reaction was followed by TLC (silica gel/hexane). After completion, the excess dissolved ozone was purged with nitrogen and treated with dimethyl sulfide (4 mL excess) and the mixture allowed to warm up to room temperature. The solvent was removed, and the residue was extracted with ether, washed with water, and dried over sodium sulfate. On removal of the solvent and sublimation, the aldehyde was obtained as a white crystal (1.48 g, 80%): mp 223–225 °C [lit.[38] mp 222–223 °C]; ^{1}H NMR ($CDCl_3$) δ 9.35 (s, formyl), 2.1 (s, methyl); IR ($CHCl_3$) 2580, 1740 cm^{-1}. The aldehyde was sensitive to air and on storage was gradually converted to methyl-*o*-carborane.

1-Methyl-2-formyl-*o*-carborane Tosylhydrazone. 1-Methyl-2-formyl-*o*-carborane (0.94 g, 0.005 mol) was dissolved in methanol (25 mL). *p*-Toluenesulfonyl hydrazide (0.95 g, 0.0005 mol) was added, two drops of concentrated hydrochloric acid added, and the mixture refluxed for 5 h. Hot distilled water was added until the mixture turned turbid. The tosylhydrazone crystallized on cooling (1.24 g, 69%). Recrystallization from methanol yielded an analytical sample: mp 165–166 °C; ^{1}H NMR ($CDCl_3$) δ 8.95 (br s, 1, –NH), 7.85–7.3 (q, 4, aromatic H), 7.2 (s, 1, –CH), 2.45 (s, 3, tolyl methyl), 1.8 (s, 3, carborane methyl); IR (Nujol) 3220, 2580, 1600 cm^{-1}. Anal. Calcd for $B_{10}C_{11}H_{22}N_2O_2S$: C, 37.08; H, 6.18. Found: C, 37.28; H, 6.28.

1-Methyl-2-(diazomethyl)-*o*-carborane. 1-Methyl-2-formyl-*o*-carborane tosylhydrazone was converted to its sodium salt by treatment with sodium hydride in THF as outlined previously. The dry sodium salt was pyrolyzed at 70–90 °C in a Kugelrohr oven as before, and the diazo compound was collected and purified by rapid chromatography on neutral alumina using pentane as eluent: ^{1}H NMR ($CDCl_3$) δ 4.2 (s, 1, methine H), 1.95 (s, 3, methyl); IR ($CHCl_3$) 2580, 2080 cm^{-1}.

General Procedure for Flash Vacuum Pyrolyses (FVP). The pyrolysis was conducted in a quartz tube (30 cm) wrapped with nichrome wire and insulated by asbestos cement. The tube was calibrated with a pyrometer prior to use. The tube, maintained horizontally, was connected by a short sleeve (heated by heating tape) to a flask containing either a diazo compound or its precursor tosylhydrazone salt. The other end of the tube was connected via a trap cooled in liquid nitrogen to a conventional vacuum line consisting of a mechanical pump and an oil diffusion pump capable of attaining 10^{-4} torr. The entire system was evacuated and the tube raised to the desired temperature rapidly (400–500 °C). The flask containing the diazo compound or its precursor was warmed gently by an oil bath at a rate that the system pressure did not rise above 10^{-3} torr. After the pyrolysis was complete, the system was cooled and opened to nitrogen. The contents of the cold trap were dissolved in an organic solvent (some polymeric product formed at this point) and subjected to analytical and preparative GC.

FVP of 1-Methyl-2-(diazomethyl)-*o*-carborane. FVP of 1-methyl-2-(diazomethyl)-*o*-carborane yielded, besides the azine, four products, three of which were identified by comparison of NMR and IR spectra with those of authentic compounds and GC retention times (coinjection) as 1-methyl-*o*-carborane, 1,2-dimethyl-*o*-carborane, and 1-vinyl-*o*-carborane. These assignments were also supported by the GC/MS of the pyrolysate. The fourth product was identified as cyclobuta-*o*-carborane: precise mass calculated for $C_4B_{10}H_{14}$ 172.2026, found 172.1916; mp 261 °C (sealed tube); ^{1}H NMR ($CDCl_3$) δ 2.9 (s); ^{13}C NMR (acetone-d_6) δ 79.68, 36.39 (J = 149.03 Hz, ^{13}C–H); IR 2980, 2605 cm^{-1}. It can be recovered unchanged after heating in a sealed tube (vacuo) at 350 °C.

Synthesis of Labeled Compounds. Vinyl-*o*-carborane was alkylated as before using ^{13}C-labeled methyl iodide (45% enrichment, 90% enriched sample from Prochem, mixed 1:1 with unlabeled methyl iodide) to yield labeled 1-methyl-2-vinyl-*o*-carborane. ^{1}H NMR shows ^{13}C satellites at δ 2.7 and 1.2 (recall δ 1.8 is carborane methyl), indicating enrichment at ~45%. Ozonolysis leads to the labeled aldehyde which was converted to the tosylhyrazone without purification. The ^{1}H NMR of the tosylhydrazone shows ^{13}C satellites at δ 2.55 and 1.05 (recall δ 1.8 is carborane methyl), still showing enrichment of ~45%. The tosylhydrazone was converted to the sodium salt by treatment with sodium hydride as before. Flash vacuum pyrolysis of the diazo compound formed in situ led to vinyl-*o*-carborane with a single enhanced peak in the ^{13}C NMR at δ 122.8. The cyclobuta-*o*-carborane isolated had a single enhanced peak in ^{13}C NMR at δ 36.35.

Photolysis of 1-Methyl-2-(diazomethyl)-*o*-carborane. The diazo compound was dissolved in ether, degassed by the freeze–thaw method, and irradiated by a 450-W Hanovia medium-pressure lamp through Pyrex. A complex mixture resulted which, on gas chromatography (3% OV-17, on 80/100 gas-chrom Q, 6 ft, 110 °C), showed the presence of cyclobuta-o-carborane and absence of vinyl-*o*-carborane.

***m*-Carborane.** *o*-Carborane was sublimed (100 °C) and carried by a slow nitrogen stream (flow rate 120 mL/min) into a 30-cm quartz pyrolysis tube heated to 640 °C. The product was collected in a cold trap. When the reaction was complete, the *m*-carborane was washed out with methylene chloride and concentrated by rotary evaporator. The reaction was quantitative.

***m*-Carborane Carboxaldehyde Diethyl Acetal.** A solution of 6.4 g (0.044 mol) of *m*-carborane in 100 mL of benzene was heated to 70 °C under argon atmosphere. At this temperature 18 mL of an *n*-butyllithium solution (2.4 M in *n*-hexane) was added. Within 0.5 h a white precipitate formed. The mixture was cooled to room temperature, and 8.6 g (0.044 mol) of diethyl phenyl orthoformate was added. The solution turned orange. The mixture was refluxed for 10 h. The solids were filtered by suction and washed with *n*-hexane. The hexane solution was passed through an alumina column. After removal of the solvent 9.04 g of a clear liquid was obtained. Pure material was obtained by preparative GC:[39] ^{1}H NMR ($CDCl_3$) δ 1.88 (t, 6), 3.75–3.41 (q, 4), 4.34 (s, 1).

***m*-Carborane Carboxaldehyde.** The diethyl acetal (9.04 g) was refluxed without further purification with 20 mL of glacial acetic acid and 20 mL of concentrated hydrochloric acid for 14 h. After cooling it was poured into water and extracted with *n*-hexane. The combined hexane extracts were washed with potassium carbonate solution, dried over anhydrous potassium carbonate, and concentrated. A white solid (6.50 g) was collected:[39] IR 2600 (B—H), 1735 (C═O) cm^{-1}.

***m*-Carboxaldehyde Tosylhydrazone.** The aldehyde was unstable and therefore used without further purification. It was refluxed with 4.8 g of tosylhydrazine in 45 mL of methanol for 3 h. Two drops of concentrated HCl was added to catalyze the reaction. The reaction was then poured into excess water and extracted with ether. The ethereal solution was dried over $MgSO_4$ and evaporated. The tosylhydrazone was chromatographed on a silica gel column eluted with a mixture of 20% ether in *n*-hexane. It was then recrystallized from a mixture of ether and *n*-hexane: yield 5.5 g; mp 150–154 °C; IR (Nujol) 3180, 2600, 1598 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.52 (s, 1, NH), 7.70–7.37 (2 d, 4), 7.07 (s, 1, CH), 2.38 (s, 3, CH_3).

Anal. Calcd for $B_{10}C_{10}H_{20}N_2O_2S$: C, 35.28; H, 5.92. Found: C, 35.46; H, 5.97.

***m*-Carboranyldiazomethane.** A solution of 1 g (0.0294 mol) of the tosylhydrazone in 15 mL of THF (dried over $LiAlH_4$) was cooled by a Dry Ice/acetone bath. To this was added 3 mL of a 1 M NaH suspension in THF (50% dispersion in oil, prewashed with *n*-pentane) with stirring under argon. A white precipitate formed. The temperature was slowly raised to ambient. Small gas bubbles were observed. THF was removed by rotary evaporation and the residue sublimed under vacuum at ~70 °C in a Kugelrohr oven. The unstable yellow diazo compound was collected in a multibulb trap cooled by Dry Ice. The apparatus was vented with argon after the reaction was finished.

General Procedure for Photolysis of *m*-Carboranyldiazomethane in Olefins. The diazo compound was washed directly from the cold trap using cold olefins and placed under an argon atmosphere. The mixture was placed in a 10-mm Pyrex tube and sealed with a Teflon stopcock. Photolyses were performed by a 450-W Hanovia medium-pressure mercury arc. Photolysis was stopped when the yellow color of the diazo compound disappeared. Products were isolated by GC.

Irradiation of *m*-Carboranyldiazomethane in *trans*-2-Butene. Diazo compound produced from 1.0 g of tosylhydrazone was dissolved in ca. 10 mL of *trans*-2-butene and irradiated until the yellow of color disappeared. The major product, the trans adduct **4a**, was found in 25% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (br s, 1, carborane H), 2.0–3.1 (m, B-H), 1.20 (d, 3, J = 6.8 Hz, methyl), 0.98 (d, 3, J = 5.9 Hz, methyl), 0.90 (m, 1, cyclopropyl), 0.65 (m, 1, cyclopropyl), 0.45 (d of d, 1, J = 12.0, 6.1 Hz, H_a); ^{13}C NMR ($CDCl_3$) 30.36, 24.89, 23.69, 18.66, 12.70 ppm; precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2500.

A second cyclopropane, the cis/anti adduct **4b**, was formed in 2% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (br s, 1, carborane H), 1.9–3.0 (m, B-H), 0.94 (d, 6, J = 5.9 Hz, methyl), 0.83 (m, 2, cyclopropyl), 0.55 (t, J = 4.76 Hz, H_a); ^{13}C NMR ($CDCl_3$) 31.98, 21.15, 11.99 ppm; precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2508.

An insertion product, **5**, was also formed in 6% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.4 (m, 1, vinyl), 5.25 (m, 1, vinyl), 2.87 (1 carborane H), 1.8–3.1 (m, B-H), 1.9–2.2 (m, 4, methylene), 1.60–1.58 (d of d, 3, methyl); precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2510.

Irradiation of *m*-Carboranyldiazomethane in *cis*-2-Butene. Diazo compound produced from 0.5 g of tosylhydrazone was dissolved in ca. 10 mL of *cis*-2-butene and irradiated until the yellow color had disappared. In addition to 15% of **4b** and 1.3% **4a**, 6% of the cis/syn adduct, **4c**, was found. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (br s, 1, carborane-H), 1.9–3.2 (m, B-H), 1.25 (t, 1, J = 9.6 Hz, H_a), 1.08, 1.07 (d of

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d, 6, methyl), 0.99 (m, 2, cyclopropyl); ^{13}C NMR ($CDCl_3$) 27.6, 16.5, 7.7 ppm; precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2506.

In addition, 3.7% of **6**, the product of C-H insertion, was found: ^1H NMR (400 MHz, $CDCl_3$) δ 5.43 (m, 1, vinyl), 5.20 (m, 1, vinyl), 2.89 (br s, 1, carborane H), 2.0–3.1 (m, B-H), 2.07 (m, 2, methylene), 1.93 (m, 2, methylene), 6.25 (br, d, 3, methyl); precise mass calcd for $C_7B_{10}H_{20}$ 214.2496, found 214.2498.

Photolyses of Cyclopropanes (4a). Approximately 3 mg of a GC-purified sample of **4b** was dissolved in 500 mL of $CDCl_3$ in an NMR tube. It was photolyzed with a Hanovia lamp for 5.5 h. The solution turned brown. The sample was checked by NMR and GC before and after photolysis. No isomerization to other cyclopropanes was detected. Some of the material decomposed during the photolysis.

Photolysis of Cyclopropane 4b. Approximately 5 mL of a sample predominantly of **4a** was dissolved in 500 mL of benzene-d_6 in an NMR tube. It was photolyzed with a Hanovia lamp for 4 h. The sample was monitored by NMR spectroscopy and flame GC before and after photolysis. No change was found.

Photolysis of Cyclopropanes 2a and 2b. These compounds were dissolved in hexane, degassed, and irradiated with a 450-W Hanovia lamp overnight through Pyrex. Gas chromatographic analysis showed no change.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grants CHE-77-24625, CHE-77-10025, CHE-81-01212) for their generous support of this work. Throughout this work we were ably assisted by the Princeton Spectroscopy Lab and by Mary W. Baum in particular. Our thanks go to them.

Registry No. 1, 77146-03-3; **2a**, 80720-98-5; **2b**, 80779-56-2; **2b′**, 80720-99-6; **2c**, 80779-57-3; **2d**, 80721-00-2; **2e**, 80721-01-3; **2f**, 80721-02-4; **2g**, 80721-03-5; **3**, 80721-04-6; **4a**, 80721-05-7; **4b**, 80779-58-4; **4c**, 80779-59-5; **5**, 80721-06-8; **6**, 80721-07-9; **7**, 75482-33-6; **8**, 80737-44-6; **9**, 17032-21-2; **10**, 16872-10-9; **11**, 20313-28-4; **14**, 71817-60-2; 1-formyl-*o*-carborane, 20394-07-4; 1-formyl-*o*-carborane tosylhydrazone, 80737-45-7; 1-diazomethyl-2-methyl-*o*-carborane, 71823-78-4; 2,3-dimethyl-5-*o*-carboranyl-2-pentene, 80737-46-8; 1-methyl-2-vinyl-*o*-corborane, 23924-82-5; 1-methyl-2-formyl-*o*-carborane, 20669-98-1; 1-methyl-2-formyl-*o*-carborane tosylhydrazone, 80737-47-9; *m*-carborane, 16986-24-6; *o*-carborane, 16872-09-6; *m*-carborane carboxaldehyde diethyl acetal, 80737-48-0; *m*-carborane carboxaldehyde, 20692-76-6; *m*-carborane carboxaldehyde tosylhydrazone, 80737-50-4; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7; trimethylethylene, 513-35-9; tetramethylethylene, 563-79-1; *n*-butane, 106-97-8; methyl iodide, 74-88-4.

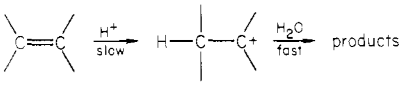
Alkene Reactivities in Trifluoroacetic Acid. A Comparison of Norbornene and Protoadamantene in Trifluoroacetic Acid and Aqueous Acid

Annette D. Allen and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada M1C 1A4. *Received October 12, 1981*

Abstract: The kinetics of the reaction of protoadamantene (**1**) and norbornene (**2**) in H_2SO_4, $HClO_4$, and CF_3CO_2H have been measured and the two alkenes are found to have similar relative reactivities, rate dependencies on acidity, solvent isotope effects, and activation parameters, independent of the particular acid. The reactivity of 2-fluoropropene (**7**) in H_2SO_4 has been measured and compared to the reactivity in CF_3CO_2H. A general correlation of the reactivity of alkenes in CF_3CO_2H and in aqueous acids is observed. These results are interpreted in terms of rate-determining proton transfer (the Ad_E2 mechanism) for all of the alkenes in aqueous acids and in CF_3CO_2H. No evidence for the intervention for π complexes as kinetically significant intermediates was obtained. This is contrary to a reported interpretation of the reaction of **1** in CF_3CO_2H.

The hydration of alkenes in aqueous acid has been intensively studied for many years, and a consensus has emerged that this process occurs with rate-limiting protonation on carbon (the Ad_E2 mechanism, eq 1).[1,2] Exceptions to this general pattern are certain



(1)

cases where the initial protonation is reversible, so that nucleophilic attack becomes rate limiting,[3] and trimethylsilyl vinyl ethers, in which rate-limiting nucleophilic attack on silicon concerted with protonation has been proposed.[4]

Other acid systems that have been studied include neat trifluoroacetic acid (TFA),[5] TFA in CCl_4,[6] sulfonic acids in acetic acid,[5d,7] and many others, especially hydrogen halides.[8,9] The

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