Tetrahedron Letters No. 52, pp 5193 - 5196.
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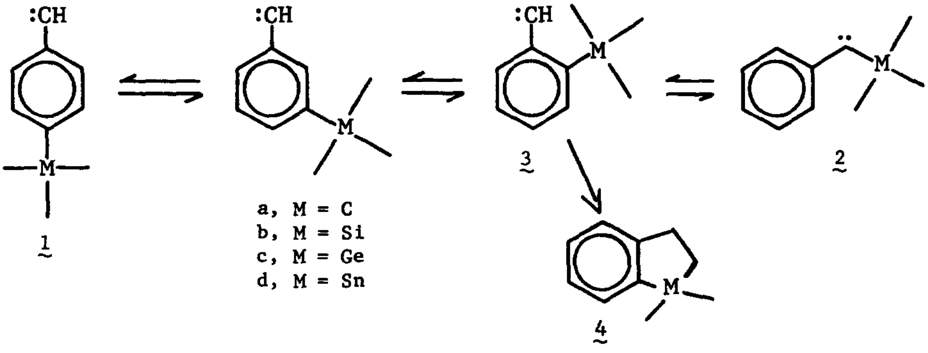
0040-4039/78/1222-5193 $02.00/0

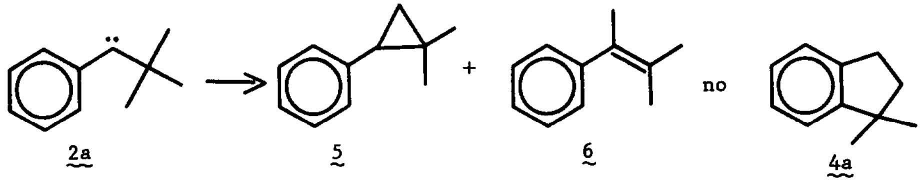
THE PHENYLCARBENE REARRANGEMENT AS A CARBENE TRANSPORT SYSTEM: GAS-PHASE REACTIONS OF *p-tert*-BUTYLPHENYLCARBENE, *p*-TRIMETHYLSILYLPHENYLCARBENE, *p*-TRIMETHYLGERMYLPHENYLCARBENE, AND *p*-TRIMETHYLSTANNYLPHENYLCARBENE

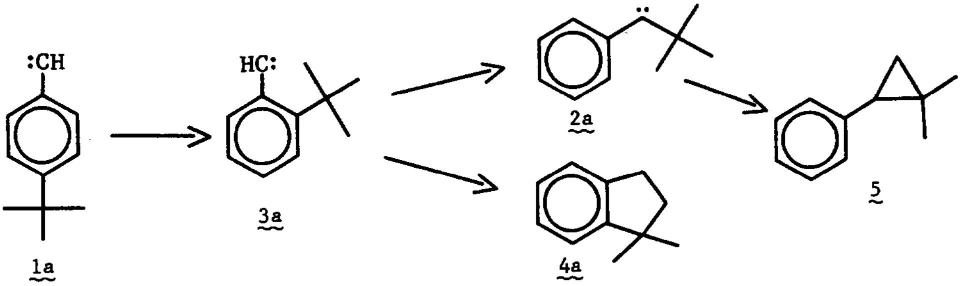
Gregory R. Chambers[1] and Maitland Jones, Jr.*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

The interconversion of substituted phenylcarbenes was discovered almost ten years ago.[2] Although much attention has been paid to the mechanistic details of the reaction,[2] it has not yet been exploited. It seemed to us that the rearrangement might serve as a way of delivering a divalent carbon from one site to another. Here we report in preliminary fashion a demonstration of the use of a benzene ring as a conduit through which a carbene can be transmitted to a remote position. We chose for this demonstration three molecules that would rearrange to known carbenes (2a-c) and one closely related but unknown system (2d). As the rearrangement from 1 to 2 is stepwise and passes through the *meta* and *ortho* isomers, a basic question to be answered was, "Is the carbene able to get past the *ortho* position, or would the *ortho* carbene 3 exclusively react with the proximate tertiary group to give a substituted indane (4a-d)?" As we shall see, the carbenes are largely, but by no means exclusively, diverted at the *ortho* stage. Thus the "delivery system" works even in non-ideal situations.

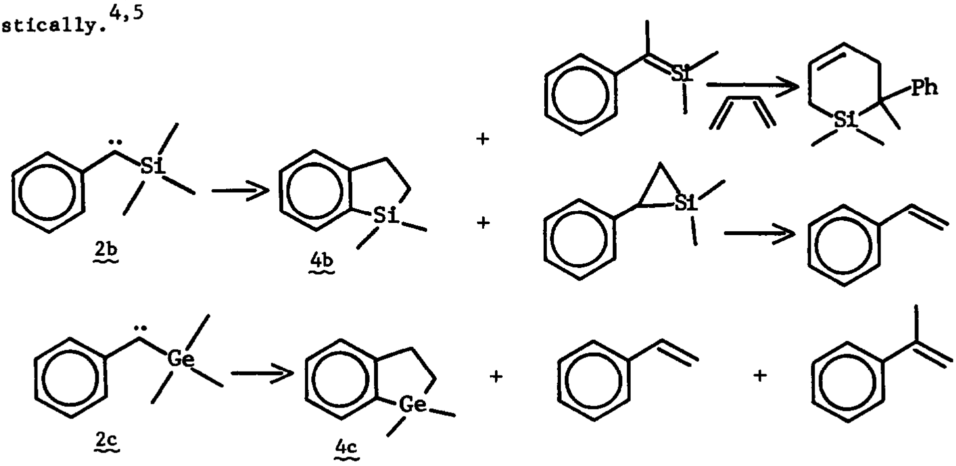


tert-Butylphenylcarbene (2a) gives 5 and 6 in the ratio 85/15.[3,4] No dimethylindane 4a is formed. This is no surprise, as carbenes are known to prefer intramolecular insertions to reaction with the benzene ring as long as they do not lead to exceptionally unstable products. *p*-*tert*-Butylphenylcarbene 1a does give 4a, doubtless through *ortho* carbene 3a, but cyclopropane 5 is also formed, proving that rearrangement all the way to 2a does occur. The small amount of 6 expected would have been obscured by the major product 4a.

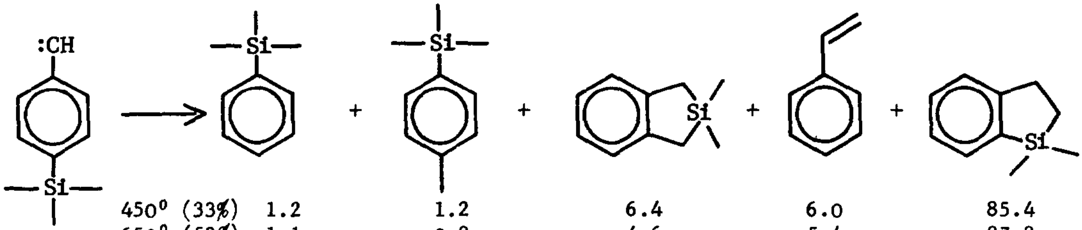




Carbene 2b has much less easy intramolecular reactions, as it must form a silirane and a silene. Therefore, it is not surprising that reaction with the benzene ring competes with these reactions, and 4b is a major product from 2b.[3] The silirane reveals itself through extrusion of dimethylsilylene to leave styrene, and the silene can be trapped with a variety of reagents.[3] Similar products are found from 2c, although no germene could be trapped and styrene was accompanied by α-methylstyrene, a compound not yet satisfactorily explained mechanistically.[4,5]

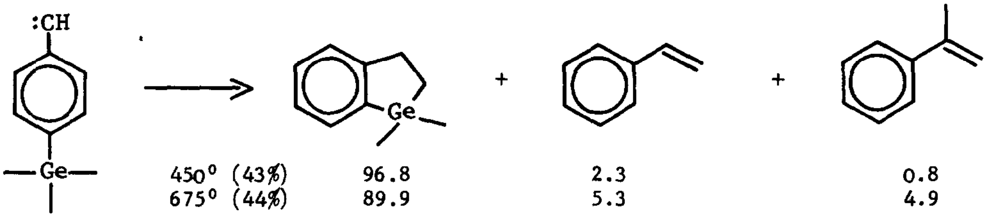


Carbenes 1b and 1c gave similar results, although more indane (4b and 4c) was produced in each case, and we have identified several other minor products. Thus the carbene center can be delivered not only to the *ortho* position where it is in a position to form the major product through carbon-hydrogen insertion, but also further to give 2b and 2c. As far as the new minor products are concerned, 2-silaindane is a known product of pyrolysis of benzyltrimethylsilane,[6] and both fragmentation and hydrogen abstraction reactions are precedented, although not widely investigated.[7]



2b

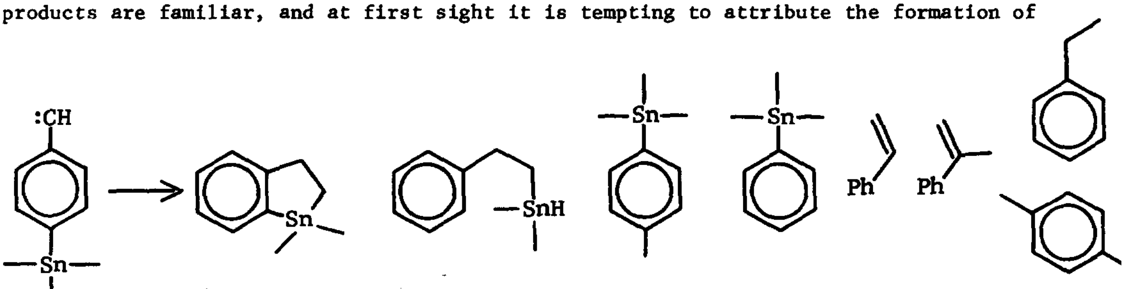
450° (33%)	1.2	1.2	6.4	6.0	85.4
650° (53%)	1.1	0.8	4.6	5.4	87.8



2c

450° (43%)	96.8	2.3	0.8
675° (44%)	89.9	5.3	4.9

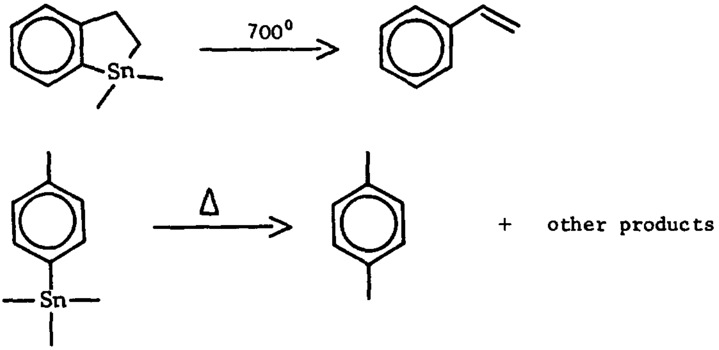
No previous reports of phenyltrimethylstannylcarbene exist. As we found it difficult to prepare phenyltrimethylstannyl ketone, we decided to approach carbene 2d through the accessible 1d. As usual, much reaction occurs from the *ortho* carbene to give 4d.[8] Other products are familiar, and at first sight it is tempting to attribute the formation of



2d

400° (17%)	55.6	4.4	5.7	2.0	26.6	1.2	4.5
500° (13%)	43.6	15.6	7.7	1.9	25.8	2.7	2.5
725° (18%)	4.2	4.1	2.4	0.6	63.6	6.3	18.8

styrene to extrusion of dimethylstannylene from an intermediate loosely described as a stannacyclopropane. However, in contrast to **4b** and **4c**,[3,5] the tin-containing compound is not stable to the reaction conditions and gives exclusively styrene at 700° C. Presumably, β-phenylethyl dimethylstannane represents partial conversion of **4d** to styrene. Only a labeling experiment will tell if *all* the styrene is produced this way. The formation of *p*-xylene and ethylbenzene is intriguing. A source of *p*-xylene is *p*-trimethylstannyltoluene, but interesting mechanistic questions still remain.[9]



REFERENCES AND NOTES

1. We thank the National Science Foundation for support of this work through Grants CHE 77-10025 and CHE 77-24625. G.R.C. is an Allied Chemical Fellow during 1978-9.
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8. All new compounds were characterized by elemental and spectral analysis.
9. G. R. Chambers, to be submitted.

(Received in USA 5 October 1978)