

THE FORMATION OF CARBON ATOMS IN THE DECOMPOSITION OF A CARBENE*

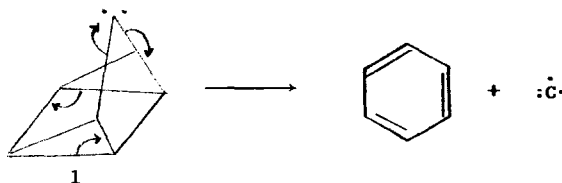
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We wish to report what we believe to be the first example of carbon atom formation by chemical reaction, specifically from the decomposition of a carbene. Carbon atoms have been generated by a number of methods including nuclear transformation,¹ carbon arcs,² pulse radiolysis,³ photolysis,⁴ flash photolysis,⁵ explosion of a graphite filament,⁶ shock heating,⁷ and plasma decomposition of simple organic compounds.⁸ The use of nuclear transformations to prepare carbon atoms results in reactive species which have excess kinetic energy in addition to being in one of the three or four lowest lying electronic states at the moment of primary reaction. The other methods noted produce carbon atoms which are essentially "kinetically thermal" but which can be in the ground electronic state or in one of the low lying electronic states.

It was our purpose to try to observe the extrusion of a carbon atom from a suitably constructed carbene. The carbene, tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]-heptane-3-ylidene ["quadricyclanilidene" (1)], may be expected to decompose to benzene and a carbon atom.⁹

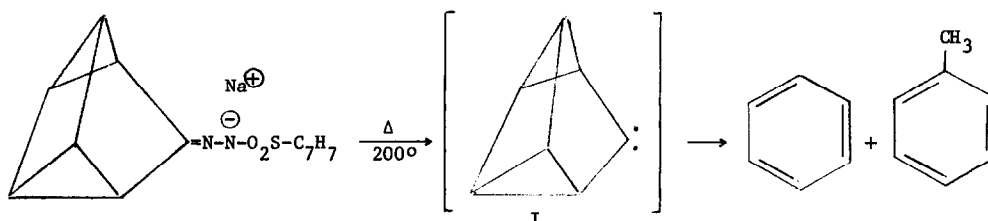


The carbene was generated by pyrolysis of the sodium salt of quadricyclanone-p-tosylhydrazone. The tosylhydrazone was prepared by reacting quadricyclanone, prepared by the method of Gassman and Patton,¹⁰ with p-tosylhydrazine in absolute ethanol.¹¹ The p-tosylhydrazone is a white crystalline solid, m.p. 184° (dec.). The infrared spectrum had maxima at 1670, 1230, 996, and 925 cm⁻¹: Anal. Calcd. for C₁₄H₁₄N₂O₂S: C, 61.30; H, 5.11; N, 10.22. Found: C, 60.03; H, 5.10; N, 9.2.

In a typical run, quadricyclanone-p-tosylhydrazone (0.2 g, 0.73 mmole) was first dissolved

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in 5 ml THF and transferred to a 50 ml flask equipped with a Teflon vacuum stopcock. A 0.1 N solution of sodium methoxide in methanol (0.73 ml, 0.73 mmole) was added dropwise with stirring under nitrogen. The THF was removed from the precipitated sodium salt on a rotary evaporator (taking care to get an even coating of the walls) and the salt dried for 1 hr under high vacuum. The evacuated flask containing the dry sodium salt was heated for 15 min in an oil bath at 200°. After approximately 2 min of heating, the white salt underwent rapid and vigorous decomposition, coating the walls of the flask with a black solid. The volatile contents of the flask were vacuum distilled into a trap. The material in the trap was analyzed by gas chromatography and identification confirmed by NMR. The two major products were benzene 12% and toluene 26% (yield based on sodium salt).



The presence of benzene as a product indicates that a carbon atom is produced. The presence of toluene is also consistent with the production of a carbon atom since it is known that carbon atoms (generated by nuclear transformations) can react with benzene to yield toluene¹²⁻¹⁴ (cf. ref. 1 for earlier work on toluene from benzene). The most probable mechanism for toluene formation in the hot atom case is from the reaction of methylene¹⁵ with benzene. However, direct insertion to give C_7H_6 which then abstracts hydrogen or insertion by CH to give C_7H_7 which then abstracts hydrogen cannot be ruled out at this stage.

The toluene could also have arisen by intramolecular rearrangement of (1) followed by hydrogen abstraction. The pathway of toluene formation was clarified by the following experiment. The pyrolysis was carried out with 87.8 mg (1.13 mmole) benzene-¹⁴C added to the salt. The toluene obtained from the pyrolysis had a specific activity of 37% of that of the labelled benzene. Assuming that 0.73 mmole of benzene are formed and that the carbon atoms react in a random¹⁶ fashion one might expect a S.A. of 61% of that of the labelled benzene. The fact that the S.A. of the labelled toluene is as high as it is (60.5% of the statistical value), is clear proof of an intermolecular reaction as major pathway.

The possibility that toluene might arise from a reaction by (1) and benzene is not ruled out by these experiments, but is unlikely on the basis of the known reaction of alkyl carbenes

(other than methylene) and hydrocarbons. However, we sought to observe another reaction which is thought to be specific for thermal carbons. Such a reaction appears to be the deoxygenation reaction observed by Skell et al.¹⁷ where carbon atoms plus tetrahydrofuran leads to ethylene and CO. Thus the pyrolysis of the sodium salt was carried out with 88 mg (1.22 mmole) of tetrahydrofuran added. In addition to benzene and toluene, ethylene (15%), CO (15%), methane (8%), and traces of C₄ products were found. The ethylene yield should be twice that of the carbon monoxide. Some of the CO undoubtedly arises from the reaction of carbon atoms with traces of oxygen remaining in the system and from the reaction of carbon atoms with methanol.¹⁸ Pyrolysis of the sodium salt in the presence of methanol gives benzene, toluene and a 31% yield of carbon monoxide. No ethylene was detected. Thus the added evidence of pyrolysis in THF clearly supports an intermolecular mechanism involving free carbon atoms.

Carbon atoms generated from the sodium salt when reacted with ethylene-¹⁴C gave low yields of a product believed to be allene by retention time correspondence on two different columns. Reactions with deposited alkanes did not produce observable products (other than the usual benzene and toluene). This is not surprising since the carbon atoms probably react more rapidly with benzene and with themselves than with alkanes or alkenes.

The mechanistic details of this reaction and the spin state of the generated carbon atom are subjects of continuing research.

References and Footnotes

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- ⁶ C. W. Spangler, S. K. Lott, and M. J. Jonich, *Chem. Comm.*, 842 (1966).
- ⁷ A. R. Fairbairn, *J. Quant. Spectros. Radiat. Transfer* **9**(7), 943 (1969).

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- ⁹ No mechanistic implication is intended in the use of the arrows in 1. The precise mode of decomposition is a subject of further study.
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- ¹³ R. L. Williams and A. F. Voigt, *J. Phys. Chem.* 73, 2538 (1969).
- ¹⁴ H. M. Pohlit, T. H. Lin, and R. M. Lemmon, *J. Amer. Chem. Soc.* 91, 5425 (1969).
- ¹⁵ The mechanism of methylene formation in the reaction of a carbon atom with a hydrocarbon is the subject of a paper (H. Elias, M. Welch, C. S. Redvanly, J. Seck, and A. P. Wolf) currently in preparation. It is apparently formed by successive removal of hydrogen (either by insertion, abstraction or stripping) from the hydrocarbon, i.e., $\dot{\text{C}} + \text{RH} \rightarrow \dot{\text{CH}} + \text{R}\cdot$; $\dot{\text{CH}} + \text{RH} \rightarrow \text{CH}_2 + \text{R}\cdot$.
- ¹⁶ It is probable that because of the high reactivity of carbon atoms with benzene, the carbon atom produced in the crystals of the sodium salt would most probably react with the in-situ formed benzene before reacting with the surface deposited benzene. The benzene-¹⁴C was introduced into the flask via a syringe. The flask was cooled and evacuated. The flask was then allowed to come to R.T. followed by recondensation of the benzene on the salt surface. The benzene-¹⁴C was therefore adsorbed, essentially uniformly, on the salt surface in addition to being in the vapor phase under the condition of the experiment. Thus one would not expect to see the statistical specific activity value of 61% of the labelled benzene.
- ¹⁷ P. S. Skell, J. H. Planka, and R. R. Engel, *J. Amer. Chem. Soc.* 89, 1748 (1967).
- ¹⁸ G. F. Palino and A. F. Voigt, *J. Amer. Chem. Soc.* 91, 242 (1969); O. Wheeler and A. P. Wolf, unpublished results. Carbon-11 atoms plus CH₃OH also yield methane.