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## A Photochemical Source of Real Alkylcarbenes<sup>1</sup>

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Abstract: Treatment of 7,7-dibromodibenzo[*a*,*c*]bicyclo[4.1.0]heptane with di-*tert*-butylcuprate or dibutylcuprate, followed by quenching with water, led to *exo-* and *endo-*7-monoalkyldibenzo-[*a*,*c*]bicyclo[4.1.0]heptanes. Photolysis through either quartz or Pyrex gave the products of intramolecular reactions of the corresponding alkylcarbenes. The temperature dependence of the products formed from *tert*-butylcarbene was verified, and butylcarbene was trapped intermolecularly.

Alkylcarbenes have presented difficulties since the first reports of their intramolecular chemistry approximately 30 years ago, and many of those problems persist today. Although surely a middle-aged discipline by now, carbene chemistry is by no means a fully understood area, and some of the most vexing points involve these simple members of this class of reactive intermediate. The residual difficulties with alkylcarbenes are especially remarkable because the early workers in the field saw the problems and considered what appears to be the correct solution almost immediately. The heroes of this story are H. M. Frey and I. D. R. Stevens, for they recognized long ago that the products of intramolecular reactions of alkylcarbenes depended upon how the precursor was decomposed. As a carbene is a carbene, some of those "carbenes" must have been something else, and these authors realized that.<sup>2</sup> Later, in an important paper, Harold Shechter returned to the issue, verified the early work, and again made the point that photolysis of diazo compounds led to a much less discriminating

intermediate than did thermal or triplet photosensitized decomposition.<sup>3</sup> Finally, Platz and his collaborators,<sup>4</sup> and others,<sup>5</sup> have now shown beyond question that reactions of excited states of diazirines<sup>4,5</sup> and diazo compounds<sup>4c</sup> complicate what had been assumed to be pure carbene chemistry. We have used the phenylcarbene rearrangement to generate phenylcarbenes unequivocally and show that even the chemistry of thermally generated carbenes is polluted by reactions of diazo compound precursors.<sup>6</sup> In order to sort out the details of simple alkylcarbene reactivity, it is necessary to have a new source not subject to the difficulties attending all nitrogenous precursors. Here we describe a promising new route to simple alkylcarbenes, and intramolecular reactions of two exemplars.

Cyclopropanated phenanthrenes give carbenes on photolysis. The parent compound, dibenzo[*a*;*c*]bicyclo[4.1.0]heptane (1), was shown to yield methylene efficiently many years ago,<sup>7</sup> and the dichloro version of this molecule, (2) was found by Chateauneuf, Johnson, and Kirchhoff to be a source of dichlorocarbene.<sup>8</sup> We have used 1,1-dibromo[*a*;*c*]bicyclo[4.1.0]heptane (3) and a



modification of the alkylation reactions of Hiyama,<sup>9</sup> in which addition of a lithium dialkylcuprate is followed by aqueous quenching, to generate mixtures of *exo-* and *endo-***4** and **5** in about 60% yield. We hoped to use these molecules as sources of *tert*-butylcarbene and butylcarbene.

*tert*-Butylcarbene has come to be a test case in alkylcarbene chemistry. Only two reactions are possible, 1,3-carbon-hydrogen insertion to give 1,1-dimethylcyclopropane (6) and 1,2-carbon-carbon insertion to give 2-methyl-2-butene (7). When *tert*-butyldiazomethane or *tert*-butyldiazirine is heated, these two products are produced in approximately 90/10 ratio. Photolysis of the diazo compound or diazirine gives quite another product ratio, approximately 50/50 (Table, entries 1-4). Indeed, it was discrepancies such as this that led to the realization that there must be at least two intermediates involved in these reactions, not just *tert*-butylcarbene. Apparently, direct rearrangement of the diazo compound leads largely to 2-methyl-2-butene. Another source of *tert*-butylcarbene, passage of 1,1-diiodoneopentane over methyllithium in the gas phase, gave a mixture of 6 and 7 in the ratio 90.2/9.8 at 21 °C (Table, entry 5).<sup>10</sup> We find that photolysis of a 90/10 *exo/endo* mixture of 4 through either

quartz or Pyrex at 25 °C led to 6 and 7 in 90/10 ratio, just as it should if the carbene were the intermediate (Table, entry 7). This demonstrates that compounds like 4 will give alkylcarbenes in sufficient amounts so that their properties can be studied.

Recently, Armstrong, McKee, and Shevlin described their studies of the carbon atom-mediated deoxygenation of pivaldehyde between -196 and -78 °C, the highest temperature practicable with their method (Table, entry 6). Remarkably, they saw 6 as the sole product.<sup>11</sup> Is the "missing" product 7 somehow the result of their reaction conditions, or is there a sharply different response to temperature of the carbon-hydrogen insertion leading to 6 and the carbon-carbon insertion leading to 7, as these authors suggested? We have run the photolysis of 4 at -78 °C, and verified that 6 is the only product at this temperature (Table, entry 8).

entr	y precursor	conditions	6	$, \succ$	ref.
1	(CH <sub>3</sub> ) <sub>3</sub> C-CHN <sub>2</sub>	130 °C	89	11	3
2	(сн₃)₃с-<_∥	145 °C	87.6	12.4	3
	<sup>N</sup>	160 °C	92	8	2
3	(CH <sub>3</sub> ) <sub>3</sub> C-CHN <sub>2</sub>	hv 25 °C	50	50	3
4	(CH₃)₃C< N N	hv	44.7	55.3	3
5	(CH₃)₃C-CHI₂ + CH₃LI	21 °C	90.2	9.8	10
6	(CH <sub>3</sub> ) <sub>3</sub> C-CHO + :C:	-78°C	100	0	11
7		<i>hv</i> 25 °C	90	10	this work
8		<i>hv −</i> 78 °C	100	0	this work

Table 1. Assorted Sources of "tert-Butylcarbene." Value of 6 + 7 normalized to 100%.

Butylcarbene is much less well studied than *tert*-butylcarbene. Two reports exist, and they are somewhat in conflict. Mansoor and Stevens found ethylcyclopropane (8) and 1-pentene (9) in the ratio 14/86 on photolysis of butyl diazomethane, and 9/91 on heating at 160 °C.<sup>2</sup> Kirmse and Horn photolyzed butyl diazomethane and obtained 8 and 9 in the ratio 25.5/74.5.<sup>12</sup> Photolysis of 5 in cyclohexene through Pyrex leads to 8 and 9 in the ratio 25/75. Note that in the formation of 9 it is not possible to distinguish 1,2 carbon-hydrogen and 1,2-carbon-carbon insertion without a label.

It is the lore of carbene chemistry that simple alkylcarbenes will react intramolecularly so fast as to preclude intermolecular trapping. However, Platz has noted that free alkylcarbenes are protected by barriers to further rearrangement,<sup>4a</sup> and suggested that they might be captured externally. So it is with butylcarbene, as we are able to detect small amounts (< 1%) of the addition product to cyclohexene, **10**, in this photolysis. Authentic **10** was made through treatment of 7,7-dibromonorcarane with dibutylcuprate. We are not yet able to find the trapping product of *tert*-butylcarbene.

These precursors are not ideal. They do give carbenes in amounts sufficient for study, but conversions are not especially high. A more serious problem is that we are not able to make dialkylcarbenes in a related way. We can convert **3** into dialkylated molecules, but photolysis leads to complex mixtures of isomers of starting material, not dialkylcarbenes. We hope to alleviate these deficiencies shortly. In the meantime, molecules such as **4** and **5** should be viable starting materials for the much-needed reinvestigation of simple and complex alkylcarbenes.

## **References and Notes:**

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