THE PHENYLCARBENE REARRANGEMENT AS A SOURCE OF REAL CARBENES.¹

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Summary: The phenylcarbene rearrangement is used to produce carbenes that are compared to the intermediates formed on photolysis and pyrolysis of diazo compounds.

WORRY that reactions of precursors might complicate chemistry thought to be characteristic of carbenes has persisted from the earliest days of carbene chemistry. It was first discovered that photolytic and thermal generation of the "same" carbene often led to very different mixtures of isomeric products derived from intramolecular insertion reactions. Kirmse's fine review of the subject in 1971² summarizes much early data. In 1979, Chang and Shechter successfully repeated some of the earlier work and added new data on photosensitized decompositions of diazo compounds and diazirines (Table 1).³ Their conclusion that relatively unselective reactions of photoexcited precursors or, perhaps, excited carbenes, were important in the photochemistry of simple carbene precursor were certainly important in the photochemical generation of "homocubylidene."⁴ Recently, overwhelming evidence has appeared that reactions of diazo compounds are important in photochemical decompositions.⁵

Table 1.		\mathbf{X}	\succ	Reference	
	hv	51	49	6,7	
	hv	45.1	54.9	3	
Ň	Δ	92	8	6,7	
	Δ	88.4	11.6	3	

In this paper we provide evidence that thermal decompositions of carbene precursors also give some products formed directly from the precursor, not from the carbene.

We first examined the products of a series of potential sources of ethylphenylcarbene. Compounds **1**, **2**, and **3** were decomposed by flash vacuum pyrolysis (FVP) at 250-500 °C. Diazo compound 1 was also photolyzed in benzene and passed in a stream of argon through a quartz tube heated to 320 °C. These experiments generate the data in the first four entries of the Table. In all cases the products consisted solely of *cis*- and *trans*- β -methylstyrene, **4** and **5**.



The product ratios were easily reproducable within 2-3% except for those from the tosylhydrazone salt **3**. Here, care must be taken to be certain that the quartz or glass surface of the FVP apparatus remains basic. Under acid conditions, a different ratio, in which the amount of trans compound **5** is increased, is found. Many years ago it was observed that strictly basic conditions gave an 20/80 mixture of **4** and **5**, whereas the carbocation gave a 5/95 ratio.⁸ We reproduce these results guite closely when the glass surface is deliberately treated with acid (Table, entries 1-4).

No phenylcyclopropane, a product that might well have been anticipated, was found. We have used a labelling experiment to ensure that this product is not formed in our gas phase reaction only to decompose to 4 and/or 5. Decomposition of deuterated tosylhydrazone salt 6 must produce 4 and 5 with deuterium in the methyl group if phenylcyclopropane is a significant intermediate. Examination of the products of decomposition of 6 by 2 H NMR revealed no detectable deuterium in the methyl groups of 4 and 5. Phenylcyclopropane is not a complicating intermediate.



These results, entries 1-4 in the Table, may represent pure carbene chemistry, pure precursor chemistry, in which Wolff-like rearrangements lead to the olefins (illustrated below only for the diazo compound), or a combination of the two processes.



Our strategy was to compare these results with those from ethylphenylcarbene generated through the phenylcarbene rearrangement.⁹ Regardless of the process by which the ring is attacked to give the initial intermediates, by the time migration to give ethylphenylcarbene is complete, the nitrogen as well as the remainder of the precursor group is surely gone. This should be a reliable source of the carbene. We again used three starting materials, compounds **7**, **8** and **9**. Indan and 2-methylstyrene, a rearrangement product of 1-methylbenzocyclobutene, were inevitable products of all three reactions, and the data in Table 2, entries **5**, **6**, and **7**, do not include these products. The ratios of **4**/5 generated in these experiments are discernibly different from those found in the earlier runs.



Finally, we used another reaction likely to generate the carbene with little or no interference from precursor chemistry, the deoxygenation of carbonyl compounds by atomic carbon.¹⁰ If we are right in our interpretation of the data, deoxygenation of propiophenone (**10**) should give the "carbene numbers." That is, the values of entries 5-7 should be reproduced, not those of entries 1-4. And so it happens; the carbonyl compound is deoxygenated by atomic carbon at 77 K to give relatively low ratios of **4**/5 (entry 8).



As the real carbene produces 5 and 4 in a 2:1 ratio, there can be no more than 75% carbene in the reactions of entries 1–3. Accordingly, it is clear that even the thermal chemistry of diazo compounds in polluted with precursor chemistry. It is not only in exotic cases⁴ that diazo compounds intrude in what was thought to be pure carbene chemistry. Simple systems are complex as well. We need a simple, unequivocal source of carbenes.

Entry	Starting Material	Conditions	4	5	Entry	Starting Material	Conditions	4	5
1	1	500 °C	24	76	5	7	500 °C	37	63
	1	320 °C (flow)	28	72	6	8	320 °C	36	64
	1	25 °C (hv,C ₆ H ₆)	23	77	7*	9	500 °C	37	63
2	2	250 °C	21	79		9	500 °C	34	66
	2	350 °C	25	75		9	500 °C	37	63
	2	500 °C	27	73	8	10	77 K	36	64
3	3	350 °C	26	74					
	3	500 °C	22	78					
4	3	acid, 500 °C	5-7	93-95					

Table 2. Ratios of *cis*- and *trans*- β -methylstyrene (4, 5) formed under different conditions.

Products are formed in yields comparable to the 50-70% reported earlier for similar decompositions¹¹ and are stable to the reaction conditions.

* These runs were carried out by three different people using different batches of 9 over a four-year span. This gives a measure of the reproducability of our data. Error analysis shows our data to be reliable \pm 1.5%

References and Notes:

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