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tert-BUTYLCARBENE FROM 1,1-DIIODONEOPENTANE[1]

Motoo Fukushima and Maitland Jones, Jr.*

Department of Chemistry, Princeton University

Princeton, New Jersey 08544

Udo H. Brinker

Abteilung für Chemie der Ruhr Universität

4630 Bochum, West Germany

SUMMARY: When 1,1-diiodoneopentane is passed through a hot tube containing methyllithium-coated Pyrex chips, 1,1-dimethylcyclopropane and 2-methyl-2-butene are produced in near quantitative yield. The ratio of products indicates that the intermediate carbene is the same as is produced from thermal or photosensitized decomposition of *tert*-butyldiazomethane but different from that formed by direct irradiation of the diazo compound.

The existence of two low-lying electronic states has complicated the analysis of the outcome of carbene reactions almost since the very discovery of the species. These days eq. 1 is generally invoked to explain products of carbene reactions. It is generally assumed that

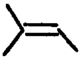
$$\begin{tikzcd} {} \arrow[r] & 1^{\circ} \arrow[r, squiggly, shift left, "k_i"] \arrow[d, "k_s"] & 3^{\circ} \arrow[l, squiggly, shift left, "k_{-i}"] \arrow[d, "k_t"] & {} \arrow[l] \\ & \text{Products} = P & \text{Products} = P^{*} & \end{tikzcd} \qquad (1)$$

thermal or photochemical generation of a carbene will yield the singlet state and the photosensitized irradiation the (usually) ground state triplet. In cases in which the two spin states equilibrate rapidly, the products are determined by the rates of product formation and usually are produced from the more rapidly reacting singlet. In other cases, however, "P" and "P*" can be formed independently, and then it is assumed that intersystem crossing between "1°" and "3°" is slow.[2]

But there are problems. For instance, many years ago it was noticed that direct irradiation of diazo compounds and/or diazirines led to less selective intermediates than thermal decomposition of the same precursors.[3] According to eq. 1 the products should be the same. Similar observations crop up even today.[4] It was Chang and Shechter who brought much needed new attention to these early results. They described careful new experiments on *tert*-butylcarbene generated in three ways from *tert*-butyldiazomethane, **1**, or the related diazirine, **2**. A similar pattern emerged from Chambers' study of intermolecular reaction of 4,4-dimethylcyclohex-2-enylidene.[6]

TABLE 1

DECOMPOSITIONS OF *tert*-BUTYLDIAZOMETHANE **1** AND 3-*tert*-BUTYLDIAZIRINE **2**. DATA FROM REF. 5

Starting Material	Conditions/ Temp (°C)			Other
2	Δ 180	88.4	11.6	
2	Δ 145	87.6	12.4	
1	Δ 130	86.8	9.9	3.2
2	hν/3° sens/25	88.4	11.6	
1	hν/3° sens/25	87.5	7.8	4.7
2	hν/25	44.7	55.3	
1	hν/25	46.5	46.7	6.7
2	hν/1° sens/25	47.3	52.7	

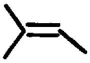
Two general explanations, both turning on the assumption that the "odd" reaction is the *direct* irradiation, have been advanced.[5,6] It is suggested that irradiation produces either an excited diazo compound whose reactions mimic those of carbenes or an excited singlet carbene. Such a species would have higher energy and hence less selectivity than the lower singlet. But it is not necessarily the direct irradiation that is abnormal. It is possible, for instance, that the thermal reaction involves diazo compounds which fortuitously give a product ratio very similar to that from the photosensitized reaction.

There are very few cases reported of thermal decompositions of diazo compounds. Presumably such experiments are rare because of a reasonable aversion to heating explosives and a desire to avoid reactions of diazo compounds. We felt it useful to find an alternative, non-diazo source of *tert*-butylcarbene in order to identify the key reaction.

Earlier this year Brinker and Ritzer described the formation of carbenes when *geminate* dibromides were passed through a heated tube packed with methyllithium-coated glass chips.[7] They were careful to show that the reactions were those of carbenes and not the carbenoids encountered when 1,1-dibromides are treated with methyllithium in solution.[7] We were not able to induce carbene reactions from 1,1-dibromoneopentane, but the related diiodide gave 1,1-dimethylcyclopropane and 2-methyl-2-butene in nearly quantitative yield when passed through the "MeLi tube" at 20-150°C. Table 2 shows the products as a function of temperature. The products are

TABLE 2

PRODUCTS FROM 1,1-DIIODONEOPENTANE AND METHYLLITHIUM

Temp (°C)			% Conversion
21	90.2	9.8	25
41	87.6	12.4	39
60	85.6	14.4	97
100	82.3	17.7	100
146	76.3	23.7	100

found in the ratio expected of the thermal or triplet-sensitized experiments of Chang and Shechter.[5] There seems nothing strange about these reactions; the curious experiment is the most simple one – the direct irradiation. Now we need to turn our efforts to a reexamination of these very simple classical experiments of carbene chemistry.

REFERENCES AND NOTES

(1) Support from the Shin-Etsu Chemical Company through a Fellowship to M.F. is gratefully acknowledged. We are also thankful for support from the National Science Foundation through Grant CHE-81-01210.

(2) For reviews of recent work see: R. A. Moss and M. Jones, Jr., in "Reactive Intermediates," Vol. 1, Wiley-Interscience, New York, 1978, Chapter 3, p. 69; *Ibid.*, Vol. 2, 1981, Chapter 3, p. 59.

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