

THERMAL DECOMPOSITION OF DIETHYL DIAZOSUCCINATE IN VARIOUS SOLVENTS;  
THE PREFERENCE OF CARBENIC PROCESS EVEN IN ACETIC ACID

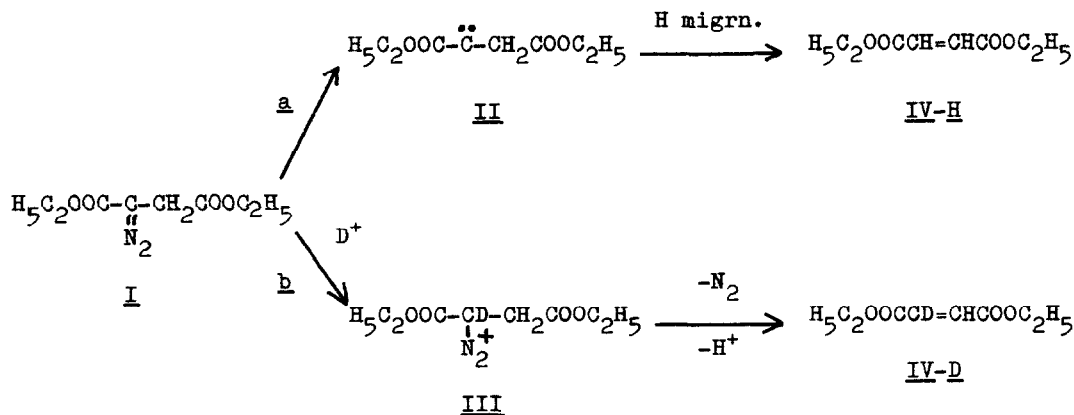
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It has been argued that the decomposition of a diazo compound proceeds through the carbene intermediate in an aprotic solvent, while it proceeds through the diazonium and/or carbonium ion in a protic medium<sup>1)</sup>. In the present letter, however, we wish to point out that the latter concept must meet with a serious reconsideration for the decomposition of diethyl diazosuccinate (I). In its olefin forming reaction, it was proved that the carbene intermediate was preferably involved even in acetic acid.

The decomposition of I<sup>2)</sup> in various solvents gives a mixture of diethyl maleate and fumarate in 30-80 % yield.<sup>3)</sup> In this olefin forming reaction, there are two possible paths, i.e., the hydrogen migration onto the carbene (path a) and beta-elimination of a diazonium ion (path b). When the decomposition is carried out in a deuterated solvent, the two paths can easily be discriminated by the analysis of the reaction products. If the olefin is resulted from path a, the incorporation of an external deuterium into the olefin would not be expected, because the process involves merely an intramolecular 1,2 hydrogen migration to the divalent carbon.<sup>4)</sup> On the other hand, path b involves a prior addition of D<sup>+</sup> from the solvent to I producing alpha-deuteriodiazonium ion (III). The beta-elimination of this diazonium ion should give the olefin (IV-D) in which the olefinic protons are 50 % deuterated if the elimination is so rapid that further replacement of the hydrogen by deuterium does not occur in the carbonium ion



intermediate.

The decomposition of I was carried out in several deuterated solvents; the resulted olefin was isolated and purified by the preparative vpc. The percentage of the deuterium incorporated into the olefinic position was determined by the nmr analysis of the purified olefin.<sup>5)</sup> In a controlled experiment, it was clearly demonstrated that the olefinic hydrogen in IV would not be replaced by a deuterium in the solvent during the reaction and isolation procedures. The results are summarized in the Table.

Table: The Percent Deuterium Incorporated into the Olefin Obtained in the Thermal Decomposition of Diethyl Diazosuccinate (I)

Solvent	Yield of Olefin <u>IV</u> (%)	% D Incorporated into <u>IV</u> (%)	% Carbenic Process Calcd. (%)
DCI-D <sub>2</sub> O	33	51 ± 3	0
Acetic Acid-d <sub>1</sub>	32	17 ± 3	66
Ethanol-d <sub>1</sub>	72	11 ± 5	78
Cyclohexanol-d <sub>1</sub>	82	4 ± 2	92

It is clearly indicated that the decomposition of I in mineral acid has undertaken solely the diazonium ion - carbonium ion process b; the olefin

produced in  $\text{DCl-D}_2\text{O}$  contained  $51 \pm 3\%$  of deuterium in its olefinic position. This proves that the replacement of hydrogen by deuterium at the carbonium ion stage does not take place even in such a highly polar solvent and the conventional concept holds good for the decomposition of I in strong mineral acid. On the other hand, the deuterium incorporation was found to be only 17% in acetic acid- $\text{d}_1$ , which figured out that only 34% of the olefin arose from the path b. The major process of the olefin formation (66%) is thus the carbenic migration process a. Moreover, the olefin resulted from the decomposition of I in cyclohexanol- $\text{d}_1$  contained only 4% of deuterium. Most of the olefin (92%) was produced via the carbene intermediate II.

Apparently, it can be concluded that the conventional concept is valid only for the decomposition of a diazo compound in strong mineral acid; the decomposition in organic acids or alcohols proceeds primarily through the carbenic migration process in spite of the fact that these solvents are evidently protic.

After these discussions, it is suggested that the acidity of the solvent might be an important factor controlling the route of the olefin forming reaction. This is found to be the case as seen in the plot of  $\text{pK}_a$  of the solvent<sup>6)</sup>

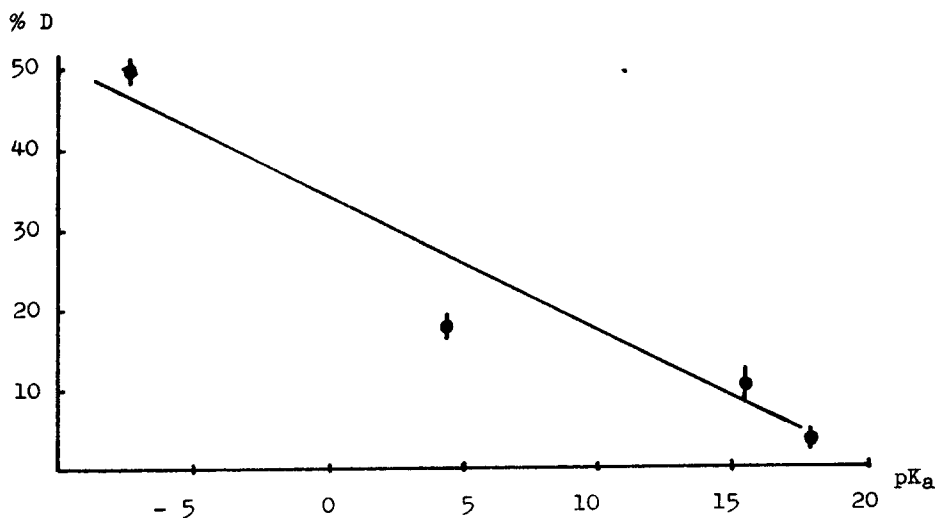


Figure: A plot of  $\text{pK}_a$  of the solvent versus the percent deuterium incorporation into the olefin.

versus the percent deuterium incorporation into the olefin. The linear relationship between them strongly indicates that the carbenic decomposition and protonation of the diazo compound compete each other in most of protic solvents in that the relative extents of both processes are a function of  $pK_a$  of the solvent.

A recent suggestion by Bayless, Friedman, Cook, and Shechter on the protonicity of the solvent in similar reactions is concerned not only with the relative acidity of the solvent but also its proton equivalence.<sup>7)</sup> They have treated the competition of the carbenic versus cationic process only for various carbinols and hence they require such a precise consideration of the solvent variations. The present investigation, however, covers far greater variation of the solvent acidity than those they studied. Consequently, it is safe to conclude that the primary important factor controlling the route of the decomposition of the diazo compound is the acidity of the solvent ( $pK_a$  value); larger the  $pK_a$  of the solvent, larger the extent of the carbenic process.

#### REFERENCES

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