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A REACTION OF BENZYLCARBENE. A COMPETITIVE STUDY OF ADDITION VERSUS HYDROGEN MIGRATION

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Thermal and photochemical decompositions of 2-phenyldiazoethane (I) are shown to give styrene (II) as a main product. The course of this reaction must involve either a hydrogen migration or a phenyl migration. This letter and the following aim to present some experimental findings which are of interest in view of their relative migratory aptitudes and the spin multiplicities of the intermediate carbenes in the rearrangement.

There have been reported several rearrangements in carbene reactions[1,2] and sequences of the migratory aptitude have been given as follows:

$$H > C_6H_5 > CH_3 \;^{1)}, \qquad SH > H > OR\ ,\ NR_2 \;^{2)}$$

However, the sequence that the migratory aptitude of hydrogen exceeds that of the phenyl has been derived from two independent observations,[1] and only a little has been known for the spin multiplicities of the intermediates in these rearrangements[3]. Accordingly, 2-phenyldiazoethane-2-d_2 (I-d) was prepared and its carbenic decomposition was investigated.

A high vacuum pyrolysis[4] ($3 \times 10^{-3} \sim 3 \times 10^{-1}$ mm) of the lithium salt of phenylacetaldehyde-2-d_2 p-toluenesulfonylhydrazone at 140° gave 2-phenyldiazoethane-2-d_2 (I-d) of 85% purity in 60% yield*. The nmr analysis of this diazo

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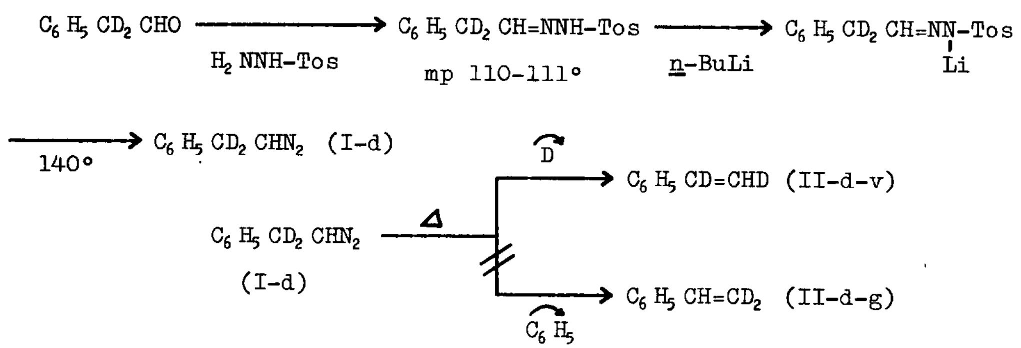
* As impurities, n-hexylbenzene (7%), styrene (5%) and 2-phenylhex-1-ene (3%) were contained.



$$C_6H_5CD_2CHO \xrightarrow[H_2NNH\text{-}Tos]{} \underset{\text{mp } 110\text{-}111°}{C_6H_5CD_2CH{=}NNH\text{-}Tos} \xrightarrow[n\text{-}BuLi]{} C_6H_5CD_2CH{=}N\underset{Li}{N}\text{-}Tos \xrightarrow[140°]{} C_6H_5CD_2CHN_2 \ \text{(I-d)}$$

$$C_6H_5CD_2CHN_2 \ \text{(I-d)} \xrightarrow{\Delta} \begin{cases} \xrightarrow{\curvearrowright D} C_6H_5CD{=}CHD \ \text{(II-d-v)} \\ \not\xrightarrow[\curvearrowright C_6H_5]{} C_6H_5CH{=}CD_2 \ \text{(II-d-g)} \end{cases}$$

compound indicates that 70% of deuterium presents at the position β to the diazo group and none at α.

The diazo compound (I-d) was decomposed thermally at a room temperature and styrene produced was isolated in 60% yield. Styrene thus obtained was purified further by a preparative vpc for the determination of deuterium distributions. The nmr analysis of this styrene exhibits 5 hydrogens at 2.75τ (phenyl), 0.3 at 3.2∼3.6τ (α-hydrogen), and 1.4 at 4.3∼4.9τ (β-hydrogen). In other words, there were found 0.7 deuterium at the position α to the phenyl and 0.6 deuterium at β*.

Since the starting diazo compound (I-d) has no deuterium at β position to the phenyl, the phenyl migration ought to give the styrene II-d-g of no deuterium at the α position. On the other hand, if a hydrogen (or deuterium) migrates to the carbene, it is expected to give the styrene II-d-v in which the deuteriums are distributed over the two carbon atoms in a ratio of 0.7 D at the α and 0.7 D at the β. The isotope effect is neglected here because it has been known that kH/kD is in an order of 1.1-1.4$^{5)}$ in similar rearrangements and hence this will not make serious change in the present predictions.

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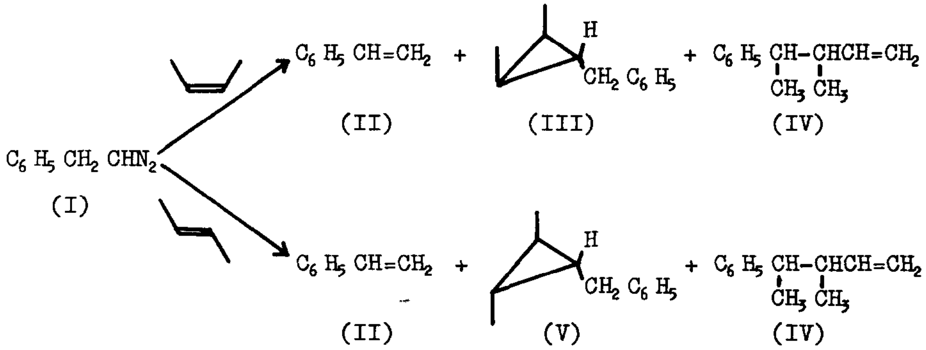
* The total amount of D in II-d was thus 1.3 D which was 0.1 D less than the amount of D in the starting I-d (1.4 D). However, the errors inherent in the relative area of nmr spectra were found to be ± 6% from three integrations. Accordingly, this discrepancy is considered to be within the experimental error.

Now, apparently the experimental finding was in a very good agreement with the value predicted from the exclusive hydrogen migration. Consequently, one comes to a conclusion that the styrene was formed only by way of the hydrogen migration and the phenyl migration does not play a role in the present rearrangement.



An irradiation of a solution of I in cis-2-butene was studied next and there were obtained 1-benzyl-cis-2,3-dimethylcyclopropane* (III) (1%), styrene (II) (39%), and 3-methyl-4-phenylpent-1-ene (IV) (13%). Similarly, an irradiation in trans-2-butene gave 1-benzyl-trans-2,3-dimethylcyclopropane (V) (3%), II (30%), and IV (10%). The addition products III and V showed satisfactory elemental analyses, IR and nmr spectra. Further confirmations of their structures were made by the comparisons with authentic samples obtained by the Wolff-Kishner reduction of isomeric 1-benzoyl-2,3-dimethylcyclopropanes prepared through known routes[6].

The thermal decomposition of I in cis-2-butene was also carried out and a similar mixture as above was obtained; III (1%), II (63%), and IV (5%).

Now, careful examinations of the cyclopropane fractions in the products were carried out by means of vpc and nmr, but no isomeric addition products were found in all cases**. Thus, it is concluded that benzylcarbene adds to a

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* Although there may be two isomers (anti and syn isomers) in III, the anti isomer was solely detected.

** The present technique can detect the presence of isomeric cyclopropane if it amounts more than 2.3%.

double bond in the stereospecific manner and hence it is presumably a singlet carbene(7). Although most of aryl carbenes have been known as the triplet(8), benzylcarbene is the singlet; an insertion of a methylene group resulted in diminution of the interaction between the phenyl and carbene.

Finally, it is to be noted that the carbene involved in the hydrogen migration might be also singlet, because there will be no reason why we should consider the different species in the hydrogen migration reaction. This problem will be considered and discussed in the following letter.

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