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INSERTION REACTIONS OF ARYL NITRENES

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Decomposition of phenyl azide in hydrocarbon solvents is known to give aniline, azobenzene, and polymeric material as the main products. It has now been found that N-alkylanilines are also formed in this reaction. For example, when phenyl azide is decomposed in cyclohexane at 180°C, N-cyclohexylaniline is produced in low yield (8%). This type of product is believed to arise by insertion of phenyl nitrene into the C-H bond of the hydrocarbon solvent.

$$C_6H_5N_3 \xrightarrow[-N_2]{180^\circ} C_6H_5\text{-}N \xrightarrow{R\text{-}H} C_6H_5NHR$$

Although Smolinsky and co-workers (1) have reported examples of the insertion of thermally generated aryl nitrenes into C-H bonds in some intramolecular reactions, our findings seem to constitute the first example of an intermolecular insertion reaction by a thermally generated aryl nitrene.

It was of interest to compare the relative reactivities of primary, secondary and tertiary C-H bonds with phenyl nitrene. With this intention, phenyl azide was decomposed in n-pentane. The amines produced in the reaction were subjected to vapor phase chromatography. Two peaks were observed with retention times of 3.5 and 10 min. These fractions were collected and identified by their infrared spectra as aniline (30% yield) and a mixture of N-pentylanilines (10% yield), respectively. Synthesis of the three possible N-pentylanilines and subsequent examination of their retention times revealed that the above N-pentylaniline mixture did not contain a detectable amount of N-(1-pentyl)-aniline (retention time 13.5 min.). However, N-(2-pentyl)aniline and N-(3-pentyl)aniline exhibited the same retention time (10 min.) and infrared absorption pattern exhibited by the N-pentylaniline mixture. The detection of the 2- and/or 3-isomer but not the 1-isomer strongly suggests that, under these conditions, insertion into the secondary C-H bonds is preferred over the primary C-H bonds by a factor of at least 100, the limitation on this value being the method of detection.

When phenyl azide was decomposed in isopentane and the basic products subjected to v.p.c. analysis, four peaks with retention times of 4 (aniline-15% yield), 7, 11, and 15 min. were observed. The relative areas of the last three peaks were 1:40:5.3. The 11-min. peak

(5% yield) has the same retention time as authentic samples of N-(2-methyl-2-butyl)aniline and N-(3-methyl-2-butyl)aniline. Collection of this fraction and examination of its infrared spectrum showed it to be a mixture of these two isomers in a ratio of 10-20:1. When this value is adjusted for the number of hydrogens involved, it can be seen that insertion into the tertiary C-H bond is preferred over the secondary C-H bonds by a factor of 20-40. The 15-min. peak from the reaction mixture has the same retention time as authentic samples of N-(2-methyl-1-butyl)aniline and N-(3-methyl-1-butyl)aniline. Unfortunately, this peak has a shoulder indicating the presence of some unidentified compound, and this makes accurate analysis impossible. Nevertheless, based on the peak areas and the adjusted number of hydrogen atoms involved, it can be seen that the ratio of insertion into the secondary C-H bonds to the insertion into the primary C-H bonds is at least 7 and probably much higher. The minor peak at 7 min. retention time has not been investigated.

The data obtained is summarized in Table I along with the data of Lwowski and Maricick on the insertion of carboethoxy nitrene into isopentane (2). As can be seen from these data, phenyl nitrene is much more selective than carboethoxy nitrene in its reactions.

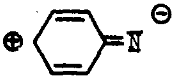
TABLE I

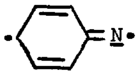
Relative Reactivities of C-H Bonds[a] with Phenyl Nitrene

Insertion Ratio	n-Pentane	Isopentane[b]
2°/1°	>100	>7(9)
3°/2°	---	20-40(3.8)

[a] Adjusted for the number of each type of hydrogens. [b] The numbers in parentheses are calculated from the data of Lwowski and Maricick (2) for the insertion of carboethoxy nitrene generated by photolysis of the azide.

The greater selectivity of the phenyl nitrene is readily explained by its greater stability as compared to carboethoxy nitrene. Although phenyl nitrene may undergo reaction either in the singlet or triplet state, both states should be stabilized by resonance with the aromatic ring:





A stabilized nitrene should lead to a higher energy of activation for the insertion reaction, and this would increase the selectivity of the nitrene.

The decomposition reactions were carried out in an autoclave at 160-180° using 10 g. of phenyl azide in 200-300 ml. of the hydrocarbon solvent. The amines formed were isolated by extraction into dilute acid solution, which was then made basic and extracted with benzene. Evaporation of the benzene gave the free amines. The mixtures were analyzed by v.p.c. on a 1/4'' x 6' Apiezon L-5% potassium hydroxide column (3) at 240°. Several of the N-pentylanilines used in this work are new compounds. They were all prepared by alkylation of aniline with the corresponding alkyl chlorides except N-(3-methyl-1-butyl)aniline which was prepared by hydrogenation of an isobutyraldehyde-aniline mixture over a Raney nickel catalyst. N-(1-pentyl)aniline was prepared both by alkylation of aniline with _n_-pentyl chloride and also by hydrogenation of a 1-pentanol-aniline mixture in the presence of Raney nickel (4). Satisfactory analytical samples were obtained by purifying the crude N-pentylanilines by v.p.c. (5).

References

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