CHEMISTRY LETTERS, pp. 1419-1422, 1981. © The Chemical Society of Japan 1981

INSERTION OF BENZOYLNITRENE TOWARD HYDROCARBON C-H BONDS

Masao INAGAKI, Tadao SHINGAKI, and Toshikazu NAGAI
College of General Education, Osaka University
Toyonaka, Osaka 560

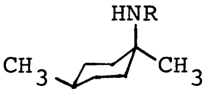
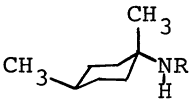
Benzoylnitrene, generated photochemically from benzoyl azide, was inserted stereospecifically into the tertiary C-H bonds of cis- and trans-1,4-dimethylcyclohexanes. The insertion regioselectivities toward the C-H bonds were determined by use of 2-methylbutane and 2,3-dimethylbutane. The insertion proceeds involving the singlet nitrene, but not the triplet, and the photo-Curtius rearrangement takes place independently of the nitrene reaction.

Mechanism of nitrene insertion toward a C-H bond depends on the electronic multiplicity of nitrene, and has been elucidated stereochemically by use of optically active or geometrical isomers as the substrates. For examples, ethoxycarbonylnitrene[1,2] and methanesulfonylnitrene[3] are known to insert toward hydrocarbon C-H bonds in their singlet states, while phenylnitrene[4] is inserted in the triplet, and cyanonitrene[5] is inserted in both of the singlet and the triplet. These nitrenes, in general, have been generated by thermal or photochemical decomposition of the corresponding azides. Benzoylnitrene from benzoyl azide(1) can be generated photochemically,[6] but not thermochemically.[7] The electronic multiplicity for the nitrene insertion, however, is not known.

A stirred solution of 1 and a hydrocarbon in dichloromethane was irradiated at 0°C by light from a low-pressure mercury lamp (mainly 254 nm) under an atmosphere of nitrogen. After the evolution of nitrogen was no longer observed, to the reaction mixture was added methanol to convert the rearrangement product, phenyl isocyanate, into its carbamate. The products were separated by use of a vapor phase chromatography, and identified by comparison of their retention times and IR and NMR spectra with those of the authentic samples.[8)] Their yields were determined chromatographically.

The results from the photolyses of 1 in trans- and in cis-1,4-dimethylcyclohexanes (DMCH) are displayed in Table 1.

Table 1. Photolyses of Benzoyl Azide[a)] in trans- and in cis-1,4-Dimethylcyclohexanes.

DMCH (mol)	CH_2Cl_2 (mol)	Product (%)[b,c)]			
				C_6H_5NCO	RNH_2
trans					
0.25	0.25	7.5	0	46	6.2
0.25	0.5	7.0	0	43	6.0
0.25	1.0	5.1	0	44	8.0
0.25	2.5	4.7	0	47	8.8
0.25	5.0	3.5	0	46	9.9
0.10	10	1.0	0	43	10
cis					
0.25	0.5	0	8.0	46	6.9
0.25	2.5	0	5.1	44	8.9
0.05	2.5	0	3.3	43	9.1

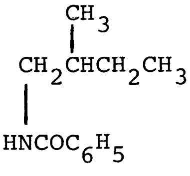
a) 10 mmol of the azide was used.

b) Calculated on the basis of the azide used.

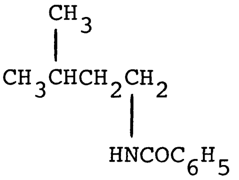
c) R ; C_6H_5CO-

Since only one tertiary insertion product isomer was isolated in each reaction even at about a 1 mol % dilution with dichloromethane,[9)] the insertion of benzoylnitrene toward the tertiary C-H bond proceeded completely stereospecifically. This fact suggests that benzoylnitrene is inserted into the C-H bonds of hydrocarbon in the singlet state only. The yields of isocyanate are practically the same despite the variation of the substrate concentration over a wide range. This constancy of the yields, independent from those of the nitrene products, means that the nitrene cannot be a precursor of the isocyanate.[6,10]

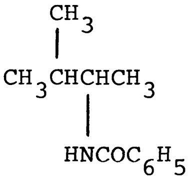
Reaction of 1 with 2-methylbutane gave four N-substituted benzamide isomers, which were formed from insertion toward the tertiary, secondary, and two types of primary C-H bonds, as shown below. From the yields calculated on the basis of


$\underset{HNCOC_6H_5}{CH_2}\overset{CH_3}{CH}CH_2CH_3$

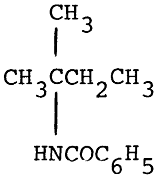
0.7 %


$CH_3\overset{CH_3}{CH}CH_2\underset{HNCOC_6H_5}{CH_2}$

0.4 %


$CH_3\overset{CH_3}{CH}\underset{HNCOC_6H_5}{CH}CH_3$

1.7 %


$CH_3\overset{CH_3}{\underset{HNCOC_6H_5}{C}}CH_2CH_3$

7.1 %

the azide used, the regioselectivity ratio for the primary (1°), secondary (2°), and tertiary (3°) C-H bonds in 2-methylbutane is estimated as 1 : 7 : 58. This ratio is considerably different from that reported by earlier investigators.[11) When the photolysis of 1 was carried out in a dichloromethane solution of 2.3-dimethylbutane, the insertion products toward the primary and tertiary C-H bonds were obtained in the yields of 1.7 % and 17.0 %, respectively. From these figures, a ratio of 1 : 60 is obtained as the regioselectivity for the primary and tertiary C-H bonds. The regioselectivity of benzoylnitrene observed in the present investigation is nearly the same as that of cyanonitrene.[12]

References

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7) The thermal decomposition gives an almost quantitative yield of the isocyanate, via a concerted mechanism,[6] in the well-known Curtius rearrangement. S. Patai, Ed., "The chemistry of the azide group," in "The Chemistry of Functional Groups," Interscience Publishers, New York (1971).

8) The carbamate was synthesized by reaction of phenyl isocyanate and methanol, the N-substituted benzamids were obtained by condensation of benzoyl chloride with four amino-2-methylbutanes and two 1,4-dimethylcyclohexylamines.

9) Although the secondary insertion products were detected vapor phase chromatographically, their yields were not determined.

10) E. Eibler and J. Sauer, Tetrahedron Lett., 1974, 2569.

11) In the reactions of benzoyl azide with 2-methylbutane and neopentane—cyclohexane mixture, the regioselectivity ratios of 1° : 2° : 3° = 1 : 77 : 965 and 1° : 2° = 1 : 391 were reported. E. Eibler and J. Sauer, Tetrahedron Lett., 1974, 2265.

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(Received April 6, 1981)