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THE RELATIVE REACTIVITIES OF AZIDOFORMATES AND SULFONYL AZIDES WITH CERTAIN HYDROCARBONS

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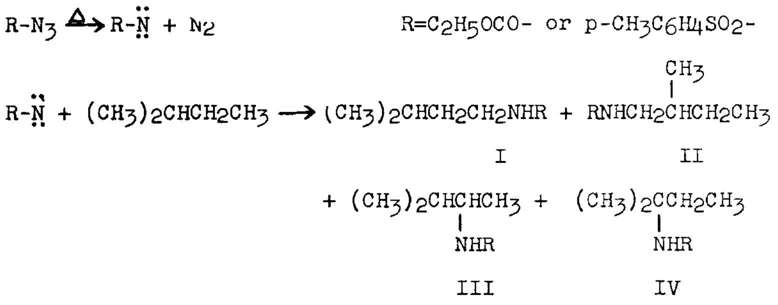
It seems well established now that both azidoformates and sulfonyl azides, when decomposed thermally, react via nitrenes, i.e., intermediates containing electron-deficient nitrogen atoms with six valence electrons (1,2,3,4,5,6). Furthermore, it has been shown that carbethoxynitrene, when generated by a non-azide route, undergoes the same insertion reactions as does the nitrene derived from ethyl azidoformate (7).

Isopentane was chosen as a representative hydrocarbon to determine the degree of selectivity of the nitrenes toward insertion into a carbon-hydrogen bond. For the reaction with ethyl azidoformate, 1-2 g. of azide was dissolved in 40 ml. of isopentane and heated in a bomb under nitrogen for four hours at 120°. The mixture was then analyzed by v.p.c., the relative areas divided by the number of available hydrogens giving the relative reactivities; peak assignments were made by comparison with authentic samples. The fact that a 2:1 ratio of II to I (R = C_2H_5OCO) was obtained consistently was a good check on the analytical procedure. In this manner the relative reactivities of primary:secondary:tertiary hydrogens towards insertion of a formylnitrene were found to be 1:10:30. Thus, a formylnitrene is a highly selective reagent.



$$R\text{-}N_3 \xrightarrow{\Delta} R\text{-}\ddot{\underset{\cdot\cdot}{N}} + N_2 \qquad R{=}C_2H_5OCO\text{- or } p\text{-}CH_3C_6H_4SO_2\text{-}$$

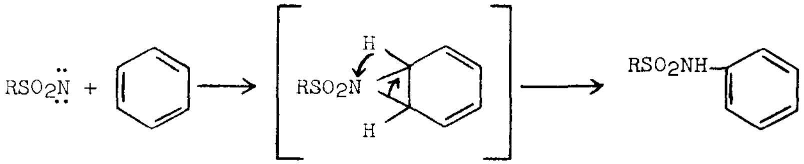
$$R\text{-}\ddot{\underset{\cdot\cdot}{N}} + (CH_3)_2CHCH_2CH_3 \longrightarrow \underset{\text{I}}{(CH_3)_2CHCH_2CH_2NHR} + \underset{\text{II}}{RNHCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3}$$

$$+ \underset{\text{III}}{(CH_3)_2CH\underset{\underset{\displaystyle NHR}{|}}{C}HCH_3} + \underset{\text{IV}}{(CH_3)_2\underset{\underset{\displaystyle NHR}{|}}{C}CH_2CH_3}$$

An attempt to determine the selectivity of a sulfonylnitrene was only partially successful, since v.p.c. could not separate the four tosylamide isomers completely. A dilute solution of p-toluenesulfonyl azide in isopentane was heated in a bomb at 155° until decomposition was complete, and the material was then analyzed by v.p.c. The ratio of III+IV:I+II ($R = p\text{-}CH_3C_6H_4SO_2$) was found to be 1.53:1. Since this ratio for azidoformates is 5.6:1, it is quite apparent that a sulfonylnitrene is less selective in carbon-hydrogen bond insertion than a formylnitrene. It seems reasonable to assume that the resonance forms available to the formylnitrene would stabilize it and make it more selective; no resonance forms, other than those involving d-orbital expansion on the sulfur, are available to the sulfonylnitrene. Both nitrenes, however, are much more selective than carbene, which attacks carbon-hydrogen bonds randomly (8).

p-Toluenesulfonyl azide was reacted with an equimolar mixture of benzene and cyclohexane by heating a 2% solution for four hours at 165°. After stripping the solvent, the residue was hydrolyzed with phenol-hydrobromic acid (9) and the resulting amines determined by v.p.c. Although the values obtained are not very precise, benzene was found to be about twice as reactive as cyclohexane. If the reaction with benzene is considered to involve addition followed by rearrangement (10), a benzene "double bond" can be considered to be eight times more reactive with a sulfonylnitrene than a carbon-hydrogen bond in cyclohexane.

$$RSO_2N_3 \xrightarrow{\Delta} RSO_2\ddot{N}: + N_2$$



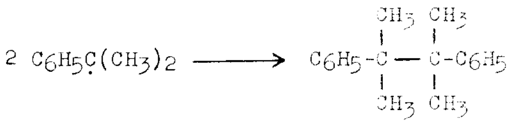
By a similar competitive experiment, ring-substitution in p-xylene has been shown to take place twice as rapidly as in benzene with a sulfonylnitrene. This might be slightly at variance with Heacock and Edmison (11), who reported no difference in reactivity between benzene and toluene, but it is in accord with a sulfonylnitrene being a highly electrophilic but non-discriminating intermediate. For comparison, p-xylene is 2500 times more reactive than benzene in electrophilic bromination (12).

According to Walker and Waters (13), p-methoxyphenyl azide reacts with cumene to give a 20% yield of dicumyl. There would appear to be little doubt that this is a free radical reaction, leading to p-anisidine and involving the triplet state of the nitrene.

$$p\text{-}CH_3OC_6H_4N_3 \xrightarrow{\Delta} p\text{-}CH_3OC_6H_4\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot + N_2$$

$$p\text{-}CH_3OC_6H_4\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot + C_6H_5CH(CH_3)_2 \rightarrow p\text{-}CH_3OC_6H_4\overset{\cdot\cdot}{\underset{\cdot}{N}}H + C_6H_5\underset{\cdot}{C}(CH_3)_2$$

$$p\text{-}CH_3OC_6H_4\underset{\cdot}{N}H + C_6H_5CH(CH_3)_2 \rightarrow p\text{-}CH_3OC_6H_4NH_2 + C_6H_5\underset{\cdot}{C}(CH_3)_2$$



$$2\ C_6H_5\underset{\cdot}{C}(CH_3)_2 \longrightarrow C_6H_5\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{-}C_6H_5$$

The same reaction has now been investigated with p-toluenesulfonyl azide, 1-pentanesulfonyl azide, and n-octadecyl azidoformate. The first gave no dicumyl, the second gave 1%, and the third gave 3%. This result is in reasonable agreement with those obtained with cyclohexane, sulfonyl azides giving less than 5% amide (2) and azidoformates giving about 20% carbamate (1). Aryl azides frequently give high yields of amine when decomposed thermally in Decalin (14). From these results it is reasonable to conclude that hydrogen abstraction is a free radical reaction which can be used as a measure of the extent of triplet reactivity of nitrenes; triplet reactivity decreases in the order ArN >-OCON >-SO$_2$N.

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