Evidence for the Involvement of Triplet Phenyl Nitrene in Intermolecular C–H Insertion

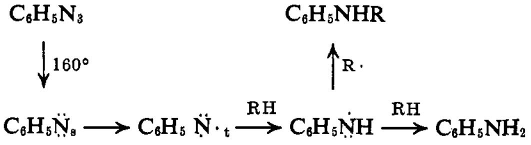
Sir:

Thermal decomposition of cyanogen azide in *cis*- and *trans*-dimethylcyclohexanes has been shown by Anastassiou[1] to give products arising from insertion of cyanonitrene into the tertiary C–H bonds. The reaction was found to be stereospecific when it was carried out in the pure hydrocarbon, but the stereospecificity was lost completely when the solution was diluted with methylene bromide.

Thermal decomposition of ethyl azidoformate in *cis*- and *trans*-4-methyl-2-pentenes was found by Lwowski and McConaghy[2] to result in the formation of a mixture of *cis*- and *trans*-aziridines. In the pure olefin the addition was nearly stereospecific, but the stereospecificity was lost on dilution with methylene chloride. More recently, carbethoxynitrene was generated in optically active 3-methylhexane and found to insert into the tertiary C–H bond with retention of configuration.[3] Furthermore, the stereospecificity did not change with the addition of inert solvent.

These observations have been explained[1,2] on the basis of the postulate that the thermal decomposition initially forms singlet nitrene which is stereospecific in its insertion and addition reactions, but which can be deactivated by collision with solvent molecules to give triplet nitrene which is nonstereospecific in its insertion and addition reactions. Further, the insertion of the singlet nitrene has been viewed as most likely proceeding through a concerted three-center transition state.[1,3]

Thermal decomposition of phenyl azide in aliphatic hydrocarbons leads to the formation of aniline, alkylanilines, azobenzene, and polymer.[4] In our attempts to account for these products, we adopted an initial hypothesis that the N-alkylaniline was formed by insertion of singlet nitrene into the hydrocarbon C–H bonds, whereas the aniline was formed from triplet nitrene by abstraction of hydrogen from solvent. (This idea was based on Lwowski's earlier report on carboethoxynitrene.[5]) To test this hypothesis, we decomposed phenyl azide in mixtures of cyclohexane and neopentane at 160°. Since insertion into the secondary C–H bonds of cyclohexane is much faster than insertion into the primary C–H bonds of neopentane, the neopentane serves as an inert solvent. The yields of the products varied erratically as the solvent composition was varied from pure cyclohexane to 25% cyclohexane–75% neopentane; however, the ratio of aniline to N-cyclohexylaniline remained constant at 4.0. This result suggested that our initial hypothesis was incorrect for, if the insertion product was formed by the singlet nitrene, addition of an inert solvent should convert some of the singlet to triplet and the amount of aniline formed should have increased. We had observed earlier that the decomposition of phenyl azide in a variety of aliphatic hydrocarbons leads to an approximately constant aniline:N-alkylaniline ratio.[4,6] Furthermore, we have found that when various *meta*- and *para*-substituted phenyl azides are decomposed in *n*-butane and in isobutane, the ratio of aniline:N-alkylaniline is a constant dependent only on the substituent and not on the hydrocarbon used. The constancy of the aniline:N-alkylaniline ratio leads to the conclusion that both of these products are being formed from the same intermediate, most likely the anilino radical.



$$\begin{tikzcd}
C_6H_5N_3 \arrow[d, "160°"] & & C_6H_5NHR & \\
C_6H_5\ddot{N}_s \arrow[r] & C_6H_5\,\dot{\ddot{N}}\cdot_t \arrow[r, "RH"] & C_6H_5\dot{N}H \arrow[u, "R\cdot"'] \arrow[r, "RH"] & C_6H_5NH_2
\end{tikzcd}$$

If, as indicated above, the N-alkylaniline is formed by a stepwise process involving a hydrogen abstraction followed by coupling of the two radicals, a large hydrogen isotope effect should be observable. To verify that this is the case, phenyl azide was decomposed in 2-methylpropane and in 2-methyl-2-deuteriopropane at 160°. The statistically corrected ratio of insertion into primary *vs.* tertiary C–H bonds was found to be 1:88 for 2-methylpropane *vs.* 1:21 for 2-methyl-2-deuteriopropane. These results indicate an isotope effect k_H/k_D of 4.1. This value is close to the observable theoretical maximum at 160°. This result clearly indicates a removal of hydrogen prior to the product-forming step. The value is much too large to be accounted for by a concerted insertion of singlet phenyl nitrene into the C–H bond.

Since the stepwise insertion process involves an alkyl free radical, one would anticipate that, if this radical is stable enough, it should be possible for it to undergo optical isomerization. To check this point, phenyl azide was decomposed in refluxing optically active 2-phenylbutane. The 2-anilino-2-phenylbutane formed (isolated by glpc) was found to be optically active. Comparison of this product with an authentic sample verified the structure. The authentic sample was resolved by recrystallization of its tartrate salt from acetonitrile. Comparison of the optically pure material with that isolated from the phenyl azide decomposition revealed that the insertion had proceeded with a maximum of 40% retention of configuration; *i.e.*, 30% of the radicals had inverted. This result is in agreement with the report of Smolinsky and Feuer[7] that intramolecular insertion in *o*-alkylphenylnitrenes proceeds with partial racemization.

In summary, the formation of aniline and N-alkylaniline in the decomposition of phenyl azide in aliphatic hydrocarbon solvents is best rationalized by involving hydrogen atom abstraction by the triplet nitrene followed either by rapid coupling of the anilino radical with the alkyl radical to give the N-alkylaniline or by abstraction of a second hydrogen to give aniline.

Acknowledgment. Acknowledgment is made to the donors to the Petroleum Research Fund, administered

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(3) W. Lwowski, Abstracts, 153rd National Meeting of the American Chemical Society, April 10–14, 1967, Miami Beach, Fla., No. O 163.

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(5) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).

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Photodesulfurization of a Sulfoxide

Sir:

Photoracemization of sulfoxides,[1] dehydrative photorearrangements of thiachroman 1-oxides,[2] and photocleavage of an episulfoxide[3] have been reported. Photochemical loss of sulfur monoxide from a sulfoxide has not been described.[4] We felt it would be of interest to attempt this type of extrusion reaction by the sensitized photolysis of *cis*- and *trans*-1,3-dihydro-1,3-diphenyl-2-thiaphenalene 2-oxides (I).[5] On sensitized irradiation, sulfoxide I did not undergo loss of sulfur monoxide but rather suffered an unusual photodesulfurization reaction.

Purified benzene solutions (0.04 *M*) of either *cis*- or *trans*-I (E_T = 58.5 kcal/mol)[6] irradiated with 366-mμ light absorbed only by benzophenone (0.055 *M*) gave rise to 1-benzoyl-8-benzylnaphthalene (II, E_T = 58.2 kcal/mol),[6] mp 139°, as the sole reaction product (80% isolated yield).[7] The structure of II was confirmed by its oxidation to 1,8-dibenzoylnaphthalene (III).[8] No photoepimerization between the two isomers of I was observed during the course of reaction.[9]

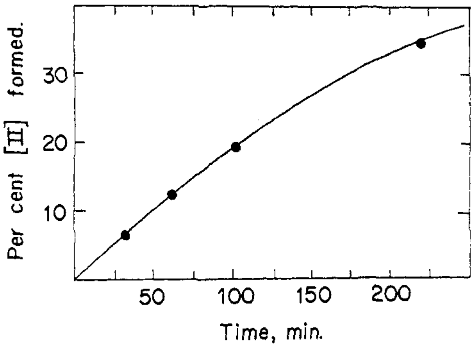
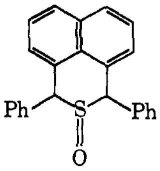


Figure 1. Plot of per cent [II] formed *vs.* time.

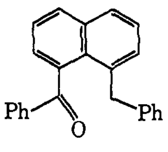
A water-cooled Hanovia Type L 450-W medium-pressure lamp fitted with Corning color filters O-52 and 7-54 was employed as the 366-mμ light source. The quantum yield for the benzophenone-sensitized decomposition of *cis*-I was found to be 0.23 while that of *trans*-I was 0.10.[10] All of the above reactions were run on a merry-go-round apparatus in sealed Pyrex tubes degassed by three freeze–thaw cycles at 10^{-5} torr. The actinometer used for these measurements was the benzophenone-sensitized isomerization of 0.10 *M* *trans*-stilbene ($\Phi = 0.43$).[11]

The decomposition of I seemed most likely to occur by initial carbon–sulfur bond rupture of the sulfoxide, giving rise to the diradical IV. We have been unable to obtain any evidence for the presence of long-lived intermediates derived from IV in this reaction. During the reaction, no significant coloration developed, and only the presence of sulfoxide, ketone, and sensitizer could be detected by careful spectroscopic and chromatographic (thin layer) examination. Furthermore, a zero-order plot of the formation of II against time using a constant intensity lamp gave a straight line, as shown in Figure 1. These results may be explained by: (1) a one-quantum process in which no long-lived intermediate is involved in the formation of ketone from IV; (2) a two-quantum mechanism which proceeds by way of a thermally stable intermediate which is photochemically transformed into ketone II. This transformation could be sensitized not only by benzophenone but also by the triplet states of sulfoxide I and ketone II, assuming the E_T value of the intermediate was <58 kcal/mol.[12]

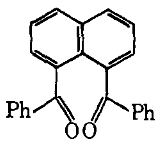
Benzophenone-sensitized irradiation of *cis*-I in benzene solution also was carried out with various concentrations of either *cis*-piperylene or 1,3-cyclohexadiene present. These data show (Table I) that with the concentrations of piperylene or cyclohexadiene which were used the reaction does not proceed through a quenchable excited state of the sulfoxide (I*). Again,



I



II



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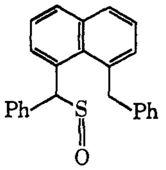

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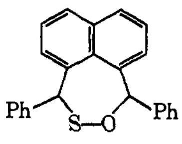
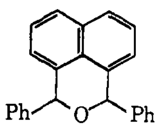


V



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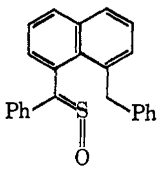
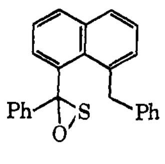


VII



VIII

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[4] For the thermal extrusion of sulfur monoxide from a sulfoxide, see R. M. Dodson and R. F. Sauers, *Chem. Commun.*, 1189 (1967).

[5] R. H. Schlessinger and A. G. Schultz, *J. Am. Chem. Soc.*, **90**, 1676 (1968).

[6] We are deeply indebted to Dr. W. G. Herkstroeter for determination of the emission spectra.

[7] All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Sulfoxide I has no absorption above 350 mμ. The same results were obtained for sulfoxide I when Michler's ketone was used as the sensitizer. Fluorenone did not sensitize the decomposition of sulfoxide I.

[8] W. Schlenk and J. Holtz, *Ber.*, **50**, 268 (1917).

[9] The base-catalyzed epimerization of *cis*-I to *trans*-I has been reported; see ref 5.

[10] Analyses were carried out using nmr. Compound II showed sharp singlet resonance for the methylene protons at δ 4.17. The nmr spectra of *cis*- and *trans*-I are given in ref 5.

[11] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[12] For analogies to this mechanism, see Robert O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1968, pp 106–154, and references cited therein.