

THE COURSE OF THE REACTION OF STYRENE AND NITROSOBENZENE: FORMATION OF  
2,3,5-TRIPHENYLTETRAHYDRO-1,2,5-OXADIAZOLE-N-OXIDES AS UNSTABLE INTERMEDIATES

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Hamer and Macaluso<sup>1</sup> have recently reported the results of a study of the reactions of nitrosobenzenes with a variety of olefins and found that no cycloadditions of the type observed by Ingold and Weaver<sup>2</sup> occurred; in each case, the only isolated product is the azoxybenzene arising by reduction of the nitrosobenzene. We have recently reinvestigated the reaction of nitrosobenzene (I) and styrene (II) and have obtained evidence for a reaction pathway which may be useful in the interpretation of the results of Hamer as well as other general studies of the reaction of I and mono-olefins.<sup>2,3</sup>

The reaction of I and II was reported<sup>2,3</sup> to be rapid leading to cleavage of the olefinic bond of II to form benzylidene-N-phenylnitronne (III); no supported mechanistic postulation was advanced and the fate of the terminal carbon was not demonstrated although formic acid could be isolated by steam distillation of the reaction residues.<sup>2</sup> These general findings were confirmed; I and II gave a highly exothermic reaction at room temperature in chloroform. At 0° in the absence of solvent and in pyridine,

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<sup>1</sup>J. Hamer and A. Macaluso, Tetrahedron Letters No. 6, 381 (1963).

<sup>2</sup>C. K. Ingold and S. D. Weaver, J. Chem. Soc. 125, 1456 (1924).

<sup>3</sup>A. Alessandri, Gazz. chim. ital. 54, 426 (1924) and earlier references.

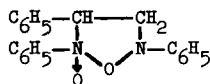
a moderate reaction without tar formation was observed and III was isolated in 25% yield. Alumina chromatography of the residues led to the isolation of azoxybenzene (IV), benzaldehyde and II; an unstable band decomposed exothermically during elution to form III. This observation suggested the existence of an unstable intermediate which was the precursor of III. Certain observations of Alessandri<sup>4</sup> and studies carried out in this laboratory on the reactions of I with methylenemalonate and 1,1-diphenylethylene<sup>2</sup> suggested that the cleavage of olefins by I to form nitrones proceeded with the formation of unstable 2:1 adducts (-N-C-C-N- structures) of I and the olefin. In order to test this postulation, the reaction of I and II was examined in greater detail.

The reaction of I and excess II was carried out at -25° for seventy-two hours; after removal of unreacted styrene by extraction, the residues were chromatographed on Florisil at 2°. Elution with ether led to the isolation of IV, benzaldehyde, III, formanilide and two yellow materials, V, m.p. 80°, and VI, m.p. 140°. Both V and VI were unstable materials and could only be maintained at low temperatures; each had satisfactory analyses [Found (V): C, 76.17; H, 5.87; N, 8.97. (VI): C, 75.30; H, 5.74; N, 8.65. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 75.45; H, 5.70; N, 8.80] and molecular weights for 2:1 adducts of I and II. The behavior of V and VI varied somewhat on decomposition, V being less stable. A spectrophotometrically dilute solution of V after four days in the dark showed bands in the ultraviolet characteristic of I and formanilide, while VI was unchanged. A similar sample of V exposed to diffuse light showed the gradual development of bands characteristic of formanilide and III, while

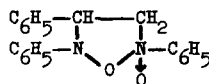
<sup>4</sup>A. Alessandri, Atti accad. Lincei 24, I, 62 (1915); Gazz. chim. ital. 55, 729 (1925).

VI only developed a band characteristic of I. The thermal decomposition of V and VI was determined by pyrolytic GLC. The chromatogram of V gave peaks identified as nitrobenzene, benzaldehyde, formanilide, and benzyldene aniline (VII); in a separate experiment, it was shown that III underwent deoxygenation under these conditions to give VII. The chromatogram of VI showed only nitrobenzene, benzaldehyde and VII. The relative yields of VII from V and VI was 20:1.

Further evidence for the structures of V and VI was provided by mass spectra. The fragmentation patterns of both V and VI showed major peaks at 318, 317, 197, 123, 121, 107 and 104; additionally, V showed a peak at 105 and VI a peak at 181. Isomeric tetrahydro-1,2,5-oxadiazole structures are consistent in all respects with the evidence cited. The NMR spectra



(V)



(VI)

of both V and VI showed benzylic, methylenic and aromatic proton signals in the relative ratios 1:2:15; the aliphatic proton splitting pattern was that of a typical  $A_2B$  system. Consistent with its attachment to the N-oxide function, the benzyl proton of V gave a signal at lower field (4.7  $\tau$ ) than the corresponding proton of VI (6.2  $\tau$ ); a similar relationship was observed for the methylene protons of VI and V. Confirmation of the positions of the N-oxide functions was provided by base-catalyzed exchange reactions; V exchanged one proton (benzylic) and VI exchanged two protons (methylenic) with  $D_2O$ . While other structures may be possible for V and VI, it is felt that they are the only reasonable structures consistent with all of the available physical and chemical evidence.

Although the decomposition studies strongly indicate V to be the precursor of III in the reaction of I and II, more definitive evidence was obtained by an infrared study of the reaction. The spectrum of a film of I in excess II showed the rapid disappearance of I and the immediate development of V over a period of seventy-five minutes; no bands characteristic of III or benzaldehyde were observed during this time period, but after ninety minutes, bands characteristic of III developed. A similar study of a mill of III and I showed that benzaldehyde was formed relatively rapidly at temperatures as low as  $-25^{\circ}$ ; this cleavage of III to azoxybenzene and benzaldehyde had previously been reported.<sup>3</sup>

These results indicate that the reaction of I and II proceeds by rapid formation of V which decomposes thermally in a slow step to yield III; III cannot be formed to any appreciable extent prior to the complete consumption of I. The other product of the decomposition is formanilide; formation of this fragment accounts for the fate of the terminal carbon of II. An internally consistent mode for the decomposition of V would require the initial formation of the unstable formylidene-N-phenylnitrene and its subsequent rearrangement to formanilide. The isomeric oxadiazole VI can also decompose to the observed products, but by a slower and more complex process.

While this study has been restricted in scope, it is probable that the reaction course postulated applies to all of the nitrosoarene olefin reactions which lead to cleavage of the olefinic bond, since these reactions are reported<sup>2,3</sup> to possess the same characteristics as the reaction of I and II.

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