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A NOVEL CYCLOADDITION OF KETENEIMINES
THE SYNTHESIS OF A 1,2-OXATHIANE

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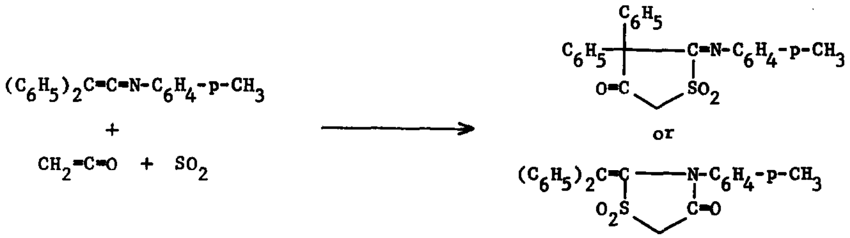
Previous studies have described the cycloaddition of a reactive species from ketene and sulfur dioxide to various imines.[1,2] The general nature of this reaction led us to

I

investigate other types of unsaturated linkages such as those present in keteneimines. Heterocumulenes are of special interest since such systems may undergo two possible modes of addition.[3,4]

We now wish to report an unusual cycloaddition of a ketene-sulfur dioxide adduct to diphenylketene-N-(p-tolyl)imine. Initially, two possible structures were formulated for the white, crystalline product, mp. 207-208°. Anal. Calcd. for $C_{23}H_{19}NSO_3$: C, 70.93; H, 4.92; N, 3.60; S, 8.23. Found: C, 70.72; H, 4.96; N, 3.72; S, 8.40.



II

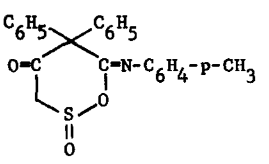
III

However, the spectral data obtained did not support either structure (II) or structure (III). The IR spectrum (KBr) of the actual product showed intense bands at 1720, 1675, and 1063 cm^{-1}.

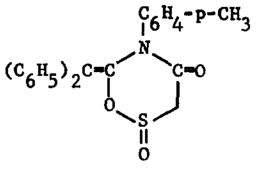
The NMR ($CDCl_3$) of the compound showed absorptions at δ2.38 (singlet, 3H), 3.57 (doublet, 1H, J=17.0 Hz), 4.08 (doublet, 1H, J=17.0 Hz), and 7.34 (multiplet, 14H).

The absence of a peak in the 1350-1300 cm^{-1} region indicated the absence of a sulfone group. This observation was supported by the fact that the two methylene protons were non-equivalent in the NMR.

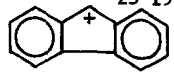
Strained ring systems containing sulfone groups have been known to undergo ring expansions.[5,6] Thus, two alternate structures (IV) and (V) resulting from ring expansion of the five-membered rings (II) and (III), could be postulated.



IV



V

The IR data did not agree with structure (V) since it showed no absorptions that could be attributed to a conjugated double bond. The absorption at 1675 cm^{-1} was too intense and its frequency too high to be attributed to a double bond of this nature. The mass spectrum of the product supported structure (IV). Peaks were observed at m/e 389, 341, 283, 194, 165, and 133. These peaks could be assigned to the following positive ions: $C_{23}H_{19}NSO_3$ (parent peak), $C_{23}H_{19}NO_2$ (loss of SO), $(C_6H_5)_2C=C=N-C_6H_4-p-CH_3$, $(C_6H_5)_2C=C=O$, , and $O=C=N-C_6H_4-p-CH_3$.

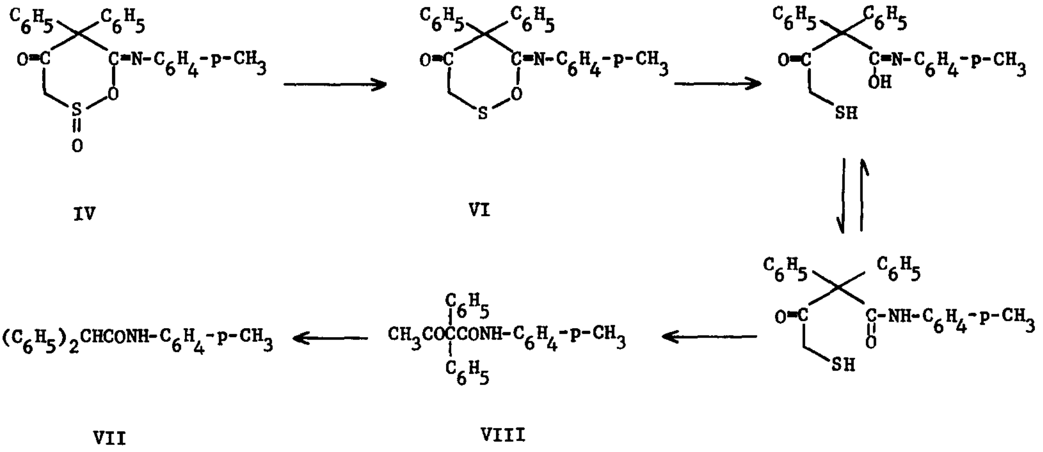
Both the IR and NMR spectra could be rationalized in terms of structure (IV). The AB quartet would be expected for (IV) because this molecule probably exists in a near chair conformation with the sulfoxide group in a preferred axial position and the methylene protons in axial and equatorial positions. The coupling constant also agreed with other geminal coupling constants.[7] The IR absorptions at 1720, 1675, and 1063 cm^{-1} could be assigned to the $>$C=O, $>$C=N-, and $>$S=O groups respectively.

The reduction of 5,5-diphenyl-6-(p-tolylimino)-1,2-oxathiane-4-one-2-oxide (IV) was also investigated. The hydrogenation of (IV) was first carried out in the presence of platinum oxide for 4 hours. The major product isolated was a white, crystalline solid, mp. 208-209°, Anal. Calcd. for $C_{23}H_{19}NSO_2$: C, 73.97; H, 5.15; N, 3.75; S, 8.58. Found: C, 73.97; H, 5.28;

N, 3.71; S, 8.66. The IR spectrum (KBr) of this product showed absorptions at 1725 (>C=O), and 1690 cm^{-1} (>C=N-). The NMR ($CDCl_3$) showed absorptions at δ2.36 (singlet, 3H), 3.55 (singlet, 2H), and 7.17 (multiplet, 14H). This data supports structure (VI). The appearance of the methylene protons as a singlet may be attributed to the more flexible ring which is formed by the reduction of the sulfoxide group.[8] This ring flips faster than the NMR time scale. Thus, the methylene protons which were non-equivalent in (IV) are now equivalent. This coalescing of the AB quartet in the NMR and the disappearence of the 1063 cm^{-1} peak in the IR with loss of one oxygen atom further supports structure (IV).

The hydrogenation of the cycloaddition product was repeated under the same conditions for 9 hours. The major product isolated was N-(p-tolyl)diphenylacetamide (VII). A trace amount of N-(p-tolyl)-α,α-diphenylacetoacetamide (VIII) was also identified.

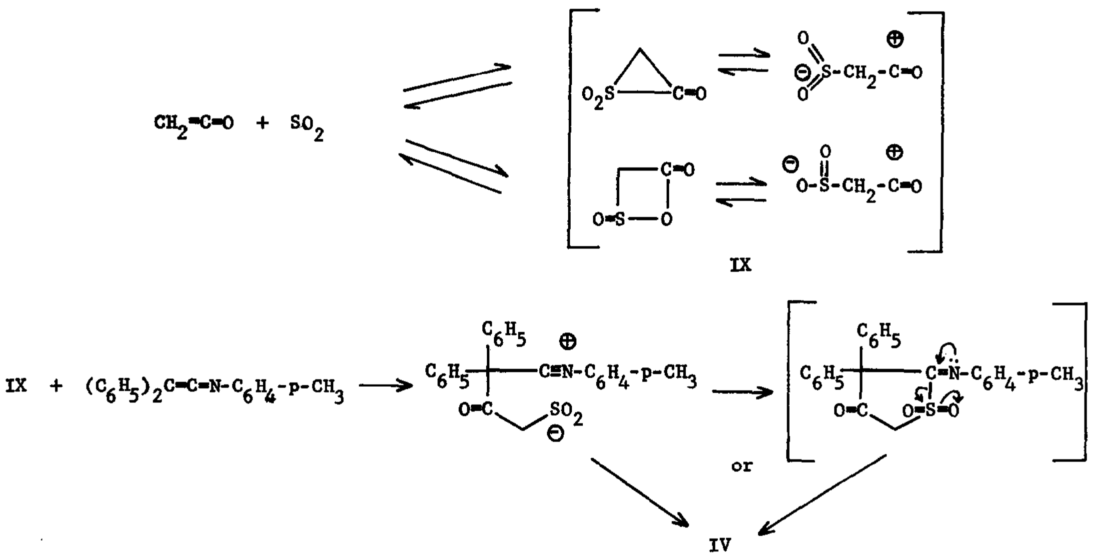
The path for the formation of the various reduction products may be postulated as follows:



5,5-Diphenyl-6-(p-tolylimino)-1,2-oxathiane-4-one-2-oxide (IV) was also treated with hydroxylamine hydrochloride to yield the corresponding oxime, mp. 164-165°.

The alkaline hydrolysis of (IV) yielded N-(p-tolyl)diphenylacetamide with the liberation of sulfur dioxide.

The formation of (IV) could be explained by the following mechanism.



Previous studies have shown that cycloadditions of the ketene-sulfur dioxide adduct always occur with the formation of a five-membered ring.[1,2] This is consistent with the greater nucleophilicity of sulfur as compared to oxygen. However, ring expansion is greatly favored in (II) because of the ability of nitrogen to donate electrons. The electrons on the nitrogen in structure (I) are not as available for neighboring group participation and hence no ring expansion occurs. An alternate route would be direct ring closure to the six-membered ring. Work is now in progress to further elucidate the mechanism of these cycloadditions.

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