

CYCLOADDITION OF KETENES WITH SCHIFF BASES V(1)  
 STRUCTURE AND STEREOCHEMISTRY OF ADDUCTS FORMED IN LIQUID SO<sub>2</sub>.

by J.M. DECAZES, J.L. LUCHE and H.B. KAGAN

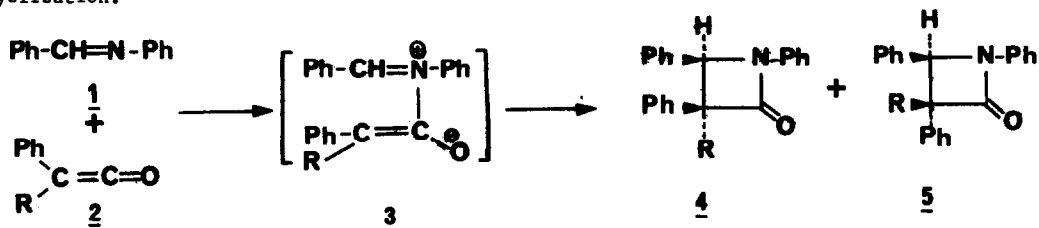
Laboratoire de Synthèse Asymétrique, Bât. 420, Université de Paris-Sud 91-ORSAY FRANCE

and R. PARTHASARATHY and J. OHRT

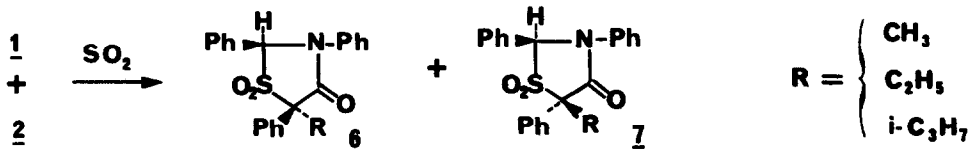
Center for Crystallographic Research, Roswell Park Memorial Institute, BUFFALO, U.S.A. N.Y. 14203

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In a previous paper (1), some of us described the stereochemical course of the addition of ketoketenes of type 2 with benzalaniline 1 and suggested that the observed stereoselectivity may be accounted for (a) by the structure of the zwitterion 3 and/or (b) by its stereoselective cyclization.



In order to obtain structural information about the dipolar species 3, we had been looking for a trapping agent, when our interest was aroused by a report of the isolation of a thiazolidinone 1-1 dioxide if ketene CH<sub>2</sub>=C=O and benzalaniline 1 reacted in liquid SO<sub>2</sub> as a solvent (2). This result suggested an extension of this reaction to ketoketenes 2.



A priori, two diastereomeric thiazolidinone 1-1 dioxides can be formed in this process. However experimental results showed that in fact, for any R, only one adduct, say A, is actually formed in 40-60% yield. NMR and TLC on the crude reaction mixture gave no evidence of the presence of two diastereomeric materials. Elucidation of the relative configuration of the compounds was undertaken to get information about (i) the mechanism of reaction in liquid SO<sub>2</sub> (ii) the

structure of a possible intermediate (3), and (iii) the stereochemical course of the SO<sub>2</sub> extrusion by photo- or thermo chemical paths which we found to yield only β-lactams. As it was necessary to have both isomers of the different thiazolidinone 1-1 dioxides, the initial sterically pure compound was epimerized (NaH in dioxane) and the mixture was separated by crystallization. The thiazolidinone-1-1 dioxides B obtained by this procedure have melting points (Table 1) and TLC R<sub>f</sub> lower than those of the corresponding A diastereomers. The chemical analyses are in agreement with the formulae. The IR spectra exhibit strong absorption at 1710 cm<sup>-1</sup> (C=O), 1335 cm<sup>-1</sup> (SO<sub>2</sub> asym. stretch.) and 1150 cm<sup>-1</sup> (SO<sub>2</sub> sym. stretch) but do not allow any characterization of the A or B series. NMR spectra exhibit clear differentiation between the A and B series, the shift of the ring proton being ~0.2 ppm larger in the B series than in the A diastereomers. A detailed discussion of the NMR spectra will not be given here as the configurations of A and B compounds could not be deduced from them.

T A B L E 1

R	CH <sub>3</sub>		C <sub>2</sub> H <sub>5</sub>		i-C <sub>3</sub> H <sub>7</sub>	
	A	B	A	B	A	B
M.P.	203-5°	198-9°	197-9°	165-7°	226-7°	208-210°

As spectral methods seemed to us unsafe, we turned to X-Ray diffraction to solve the configurational problem. Compound A (R = iC<sub>3</sub>H<sub>7</sub>) M.P. 226-7°, resulting of the addition of phenyl isopropyl-ketene on 1 in liquid SO<sub>2</sub> was investigated by X-Ray analysis. Crystals of A are monoclinic, space group P2<sub>1</sub>/c with four molecules in the unit cell. The unit cell constants at (23±2)°C are : a=12.847(4)Å, b=11.131(1)Å, c=17.230(6)Å, β=121.31(5)° (λCuKα<sub>1</sub> = 1.54051Å). Full three-dimensional data involving 4700 reflections were measured by the stationary crystal stationary counter technique on a GE XRD-6 diffractometer equipped with a scintillation counter and Ni-Co Ross filters for monochromatization. The structure was solved by direct methods using the multi-solution technique (4). The hydrogen atoms were located using electron-density difference maps. The final R-index after refinement by least squares (block-diagonal) is 0.04.

The detailed conformation of the molecule is illustrated with the perspective view (fig.1) Bond distances and angles are given in Fig. 2a and 2b. The average e.s.d. of the bonds and bond-angles not involving the hydrogens are computed to be, respectively, 0.004Å and 0.1°.

Fig. 1

Perspective view along the b axis

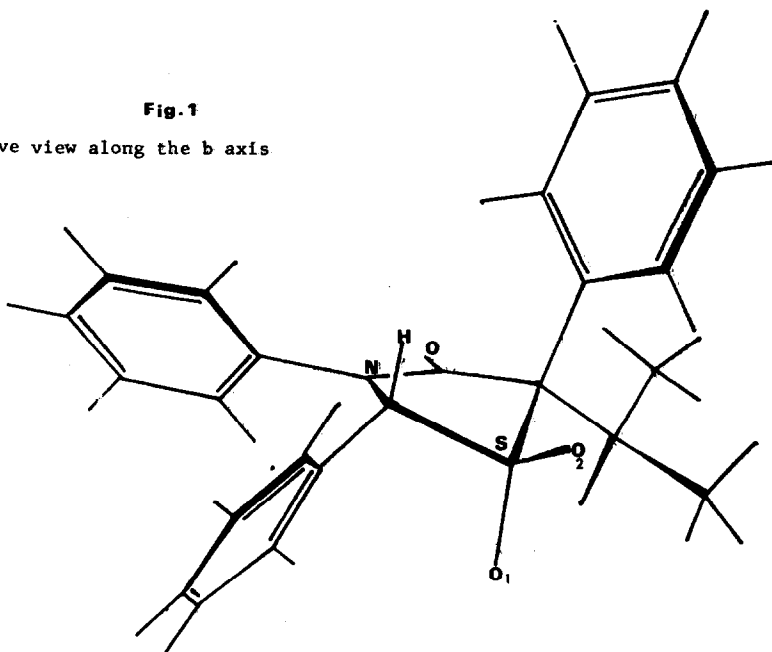


Fig. 2a

Bond distances

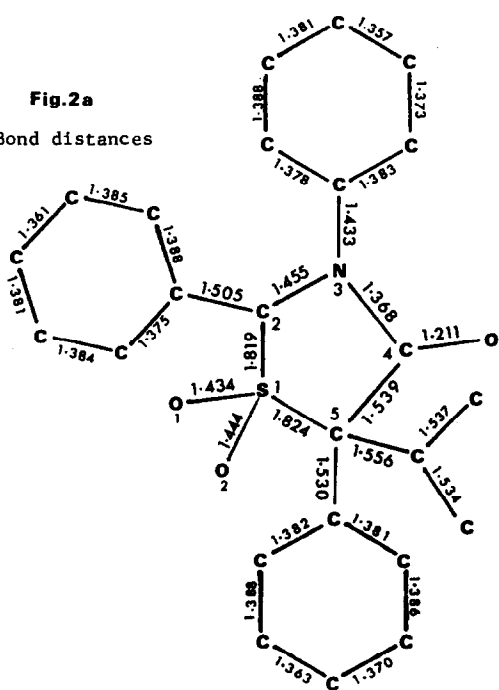
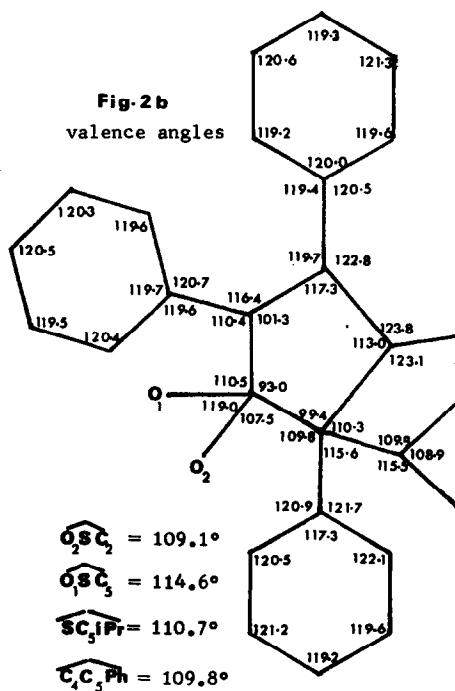


Fig. 2b

valence angles



Although the purpose of this paper is not concerned with a detailed discussion of the structure (which will be given in a next paper) some important features can be pointed out :

1°) It is clear from Fig. 1 that series A undoubtedly possesses the trans configuration 7.

Hence, the reaction of a ketene 2 with benzylidene aniline 1 in liquid SO<sub>2</sub> as a solvent yields only the trans thiazolidinone 1-1 dioxides 7.

2°) The five membered ring of these compounds is in an envelope conformation, at least in the solid state, with the sulfur atom out of the plane through the other four atoms of the ring by 0.78 Å. The distance between the axial ring hydrogen and the axial phenyl is 2.7 Å, i.e. the same order of magnitude as two axial substituents of a cyclohexanic ring. The nitrogen atom is planar, within the experimental error and this plane contains also the carbonyl group, C<sub>2</sub> and C<sub>5</sub> atoms. The lengths of C=O bond (1.21 Å) and N-C(O) bond (1.37 Å) are consistent with a conjugated amide. However, the N phenyl ring lies in a plane at 44.9° from the amide plane. Even if a rotational isomerism around the Ar-N bond occurs in the solution, it can be expected from the non-planarity of the N-Arylamide system, that its conjugation should be significantly decreased when compared to almost fully conjugated systems such as some N-Aryl β-Lactams (5,6). Spectroscopic and stereochemical studies of the thiazolidinone dioxides are now in progress and will be reported later.

#### Acknowledgement

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