

## REACTION OF DIPHENYLKETENE WITH CONJUGATED SULFILIMINES

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Cycloaddition reactions of diphenylketene (I) with N-pyridin-2-yl-S,S-dimethylsulfilimine (II), N-benzoxazol-2-yl-S,S-dimethylsulfilimine (IV), and N-benzthiazol-2-yl-S,S-dimethylsulfilimine (VI) were investigated. I reacted with II, IV, and VI giving cycloadducts, 2,3-dihydro-3-keto-2,2-diphenylimidazo[1,2-a]pyridine (IIIa), 2,3-dihydro-3-keto-2,2-diphenylimidazo[2,1-b]benzoxazole (V), and 2,3-dihydro-3-keto-2,2-diphenylimidazo[2,1-b]benzthiazole (VII) by accompanying an elimination of dimethyl sulfide, respectively.

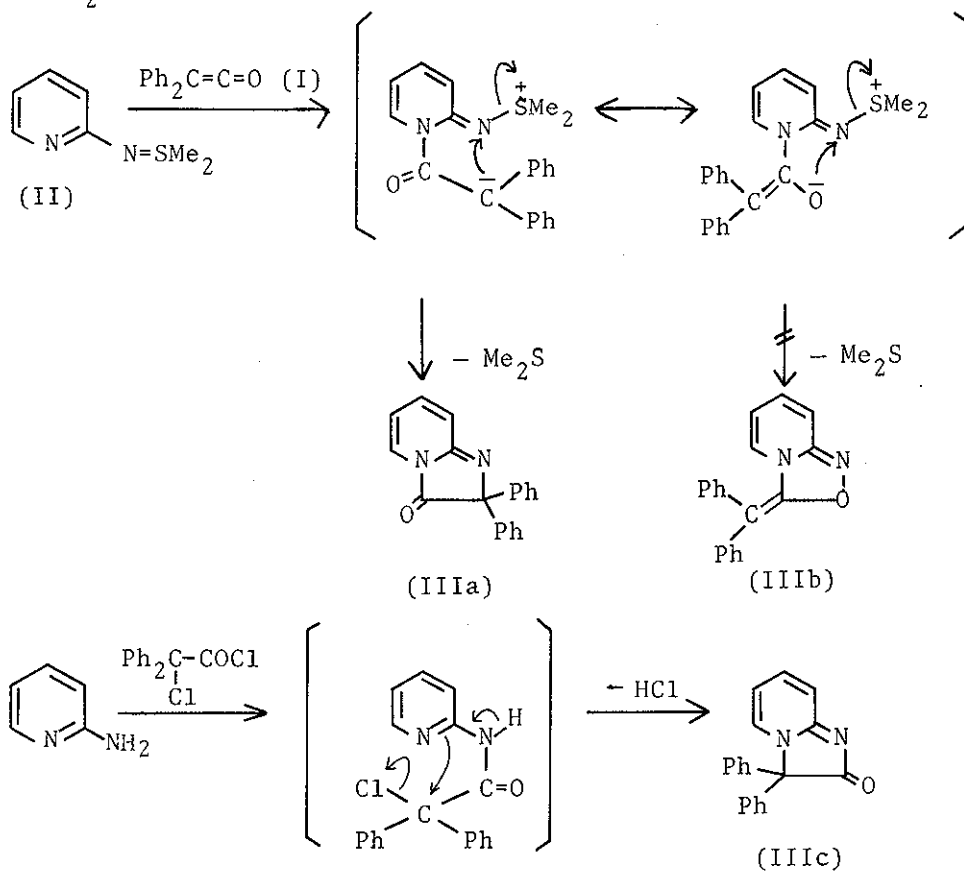
On the other hand, N-benzimidoyl-S,S-dimethylsulfilimine (VIII), contrary to our expectation, was not cyclized, but gave a Michael type adduct (IX).

Sulfilimines  $RN=SR'_2$  bearing a nucleophilic nitrogen and a good leaving group have so far been a little used in synthesis. These reactions often involve the cleavage of the sulfur-nitrogen bond and afford the products<sup>1</sup>.

The cycloaddition reactions of several heterodienes with ketene derivatives<sup>2</sup> as well as sulfilimines with dipolarophiles<sup>3,4</sup>

have been reported. In the present paper we wish to report the cycloaddition reaction of sulfilimines having a N=C-N=S double bond with diphenylketene (I).

When N-pyridin-2-yl-S,S-dimethylsulfilimine (II)<sup>5</sup> was allowed to react with an equimolar amount of I in refluxing xylene under nitrogen for 6.5 hr, colorless crystals of m.p. 214-214.5°, C<sub>19</sub>H<sub>14</sub>ON<sub>2</sub> (III) [ Mass m/e; 286(M<sup>+</sup>); PMR(CDC<sub>3</sub>Cl) $\delta$ : 6.60-6.72(1H,m), 7.17-7.62(13H,m); CMR(d<sub>6</sub>-DMSO) $\delta$ : 184.9(C=O), 166.7(C=N), 77.3 (\*CPh<sub>2</sub>) ] were obtained in 28% yield.



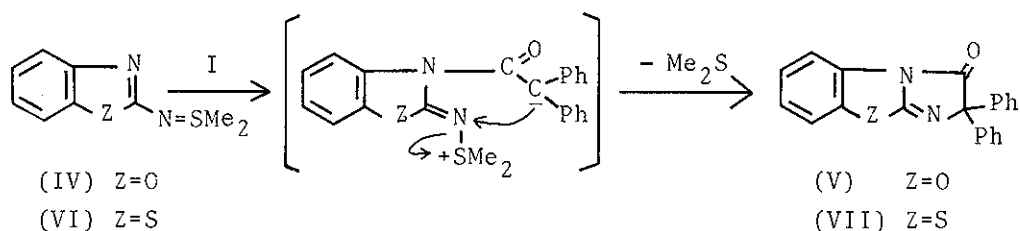
Scheme I

Of the three probable structures (IIIa-c) for the compound (III), we propose the structure IIIa is the most reasonable one on the basis of spectral data and reaction mechanism. IR spectrum of III shows absorptions at 1697 and 1627  $\text{cm}^{-1}$  due to the carbonyl and imine groups, respectively. The existence of these absorption bands contradicts the possibility of the structure IIIb. However, the possibility of the structure IIIc is undeniable.

In order to prove the structure of III, we synthesized 2,3-dihydro-2-keto-3,3-diphenylimidazo[1,2-a]pyridine (IIIc) [ m.p. 213-215°; Mass m/e: 286( $\text{M}^+$ ); PMR( $\text{d}_6$ -DMSO) $\delta$ : 7.18-7.56(14H,m); CMR( $\text{d}_6$ -DMSO) $\delta$ : 172.2(C=O), 150.6(C=N), 81.2( $\text{CPh}_2^*$ ); IR(KBr): 1764 (C=O), 1635  $\text{cm}^{-1}$ (C=N) ] in 16% yield from 2-aminopyridine and  $\alpha,\alpha$ -diphenyl- $\alpha$ -chloroacetyl chloride by using the synthetic procedure for 2-hydroxy-3-methylimidazo[1,2-a]pyridine<sup>6</sup>. In comparison of IIIc with III in the IR spectra and melting points both were different but the fragmentation pattern of the mass spectrum in IIIc was very similar to III. From these data, the structure of III was confirmed to be 2,3-dihydro-3-keto-2,2-diphenylimidazo[1,2-a]pyridine (IIIa).

N-Benzoxazol-2-yl-S,S-dimethylsulfilimine (IV)<sup>3</sup> was treated with an equimolar amount of I in xylene at room temperature under nitrogen for 36 hr to afford 2,3-dihydro-3-keto-2,2-diphenylimidazo[2,1-b]benzoxazole (V) [ m.p. 111-112°; Mass m/e: 326( $\text{M}^+$ ); PMR( $\text{CDCl}_3$ ) $\delta$ : 7.18-7.35(14H,m,ArH); IR(KBr): 1742(C=O), 1629  $\text{cm}^{-1}$ (C=N) ] in 19% yield.

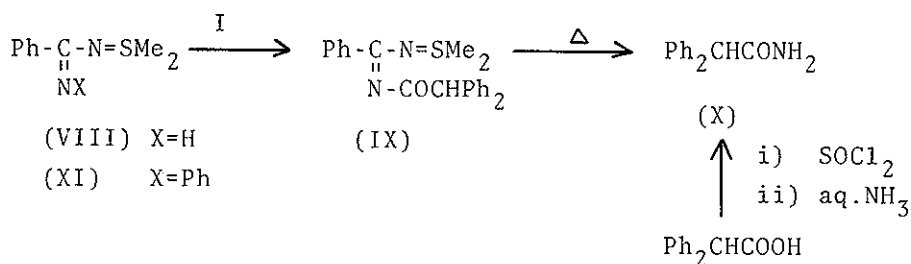
N-Benzthiazol-2-yl-S,S-dimethylsulfilimine (VI) [ m.p. 85.5-86.0°; Mass m/e: 210( $\text{M}^+$ ); PMR( $\text{CDCl}_3$ ) $\delta$ : 2.82[6H,s, $\text{S}(\text{CH}_3)_2$ ], 6.89-7.51(4H,m,ArH) ] was prepared in 43% yield by employing the same method as described in the case of IV<sup>3</sup>.



Scheme II

Reaction of VI with an equimolar amount of I in xylene at 80° under nitrogen for 8 hr gave 2,3-dihydro-3-keto-2,2-diphenylimidazo[2,1-b]benzthiazole (VII) [ m.p. 249°; Mass m/e: 342(M<sup>+</sup>); PMR(CDCl<sub>3</sub>)δ: 6.74-7.34(14H,m,ArH); IR(KBr): 1720 cm<sup>-1</sup>(C=O) ] in 22% yield.

N-Benzimidoyl-S,S-dimethylsulfilimine (VIII)<sup>7</sup> reacted with an equimolar amount of I in xylene at room temperature under nitrogen for 18 hr to give a Michael type adduct, N-(N'-diphenylaceto)benzimidoyl-S,S-dimethylsulfilimine (IX) [ m.p. 184-185°; Mass m/e: 312[M<sup>+</sup>-S(CH<sub>3</sub>)<sub>2</sub>]; PMR(CD<sub>3</sub>CN)δ: 2.67[6H,s,S(CH<sub>3</sub>)<sub>2</sub>], 5.12(1H,s,CH), 7.25-7.38(15H,m,ArH); IR(KBr): 1620 cm<sup>-1</sup>(C=O) ] in 67% yield.

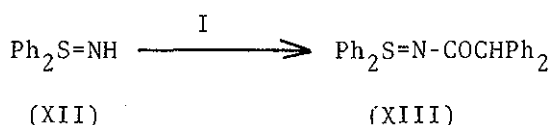


Scheme III

In order to prove the structure of IX, IX was pyrolyzed at 160° to give diphenylacetamide (X), m.p. 169-169.5°(lit.,<sup>8</sup> 166-168°), in 14% yield, whose structure of X was confirmed by the comparison

with an authentic sample<sup>8</sup> prepared from diphenylacetic acid. On the other hand, N-(N'-phenyl)benzimidoyl-S,S-dimethylsulfilimine (XI)<sup>9</sup> with I resulted in recovery of the starting materials.

An attempt was undertaken to investigate the reactivity of the S=N bond. When the reaction of S,S-diphenylsulfilimine (XII)<sup>10</sup> with an equimolar amount of I was carried out under cooling on an ice bath, diphenyl-N-diphenylacetylsulfilimine (XIII) [ m.p. 131-131.5°; Mass m/e: 228(M<sup>+</sup>-Ph<sub>2</sub>CH), 186(M<sup>+</sup>-Ph<sub>2</sub>CHCON); PMR(CDCl<sub>3</sub>)δ: 5.33(1H,s,CH), 7.15-7.65(20H,m,ArH); IR(KBr): 1606 cm<sup>-1</sup>(C=O) ] was obtained in 34% yield.



Scheme IV

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