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ADDITION OF N-CHLOROSULPHONYL ISOCYANATE TO DIPHENYLMETHYLENECYCLOPROPANE-CYCLIZATION *VIA* OXYGEN

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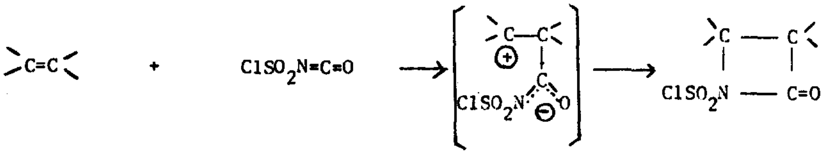
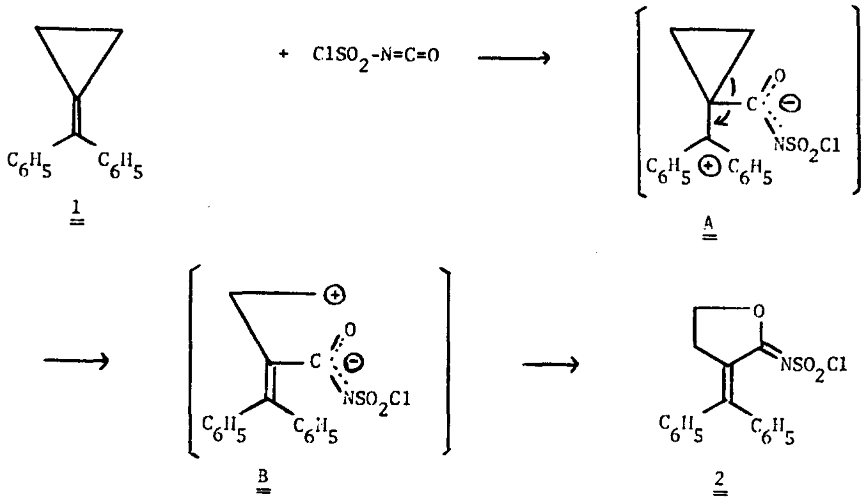
The addition of N-chlorosulphonyl isocyanate (CSI) to olefins is a very useful method for the preparation of β-lactams[1,2]. Monoolefins cyclize through nitrogen



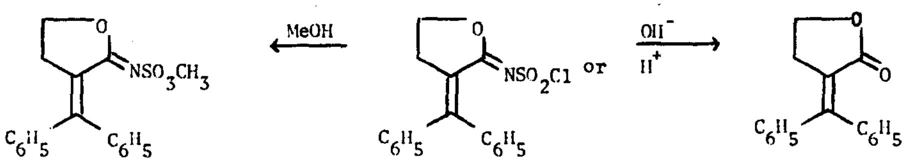
and there is only one report of a cyclization through oxygen after rearrangement to yield an iminolactone[3]. On the other hand dienes[4,5,6] and trienes[7,8] react with CSI to yield both lactones and lactams. We wish to report on the addition of CSI to a strained monoolefin, namely diphenylmethylenecyclopropane[9] (**1**) which proceeds through the unusual oxygen closure to yield an iminolactone.

A solution of 15 mmoles of CSI in CH$_2$Cl$_2$ was added to a stirred solution of 10 mmoles of **1** in the same solvent and left overnight at room temperature; the solvent was removed and the residue was triturated with dry ether to yield 85% of a single product 2, m.p. 152-156° (pure by NMR). Recrystalization from methanol gave an analytical sample[10)], m.p. 159-161° in low yield due to further reaction of 2 with methanol.

The mass spectrum, M^+ 347, 349 m/e indicated that 2 is a 1:1 adduct of CSI and 1. The presence of a strong band at 1580 cm^{-1} (>C=N-) in the IR($CHCl_3$) and the absence of any carbonyl band showed that 2 is an iminolactone and not a lactam. The UV spectrum: λ_{max}^{EtOH} (nm) 227 (ε 15200), 312 (ε 11600) and particularly the NMR spectrum:



($CDCl_3$) δ (Hz) - 7.35/m, 10H (phenyl), 4.80/t (J=7) 2H (-OCH_2-), 3.29/t (J=7) 2H (=C-CH_2-), confirmed that the product is α-diphenylmethylene-N-chlorosulphonylimino-γ-butyrolactone (2). Further proof for the structure 2 was acquired from hydrolysis and esterification reactions. When 2 was treated with 2N NaOH in water/acetone-α-diphenylmethylene-γ-butorylactone (3), m.p. 169-170° (methanol or cyclohexane) was obtained in 40% yield. This hydrolysis could also be achieved with methanolic HCl in 70% yield, but the product was contaminated with a methyl ester of 2. γ-Lactone 3 has the following spectral properties: ν_{max}^{nujol} (cm^{-1}) 1750 (α,β-unsaturated γ-lactone); λ_{max}^{EtOH} (nm) 223 (ε 15000), 281 (ε 12000); NMR (CDCl$_3$) δ (Hz) - 7.30/m, 10H (phenyl), 4.30/t (J=7) 2H (-OCH$_2$-), 3.10/t (J=7) 2H (=C-CH$_2$-) and mass spectrum M$^+$ 250 m/e. Refluxing 2 with methanol for 1 hour gave mainly the sulphonester 4 (contaminated with



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3), m.p. 153-155° (methanol); ν_{max}^{nujol} (cm^{-1}) 1620 (C=N-); λ_{max}^{EtOH} (nm) 227 (ε 15000), 301 (ε 11500); NMR: (CDCl$_3$) δ (Hz) - 7.35/m, 10H (phenyl), 4.59/t (J=7) 2H (-OCH$_2$-), 3.30/s, 3H (-SO$_3$CH$_3$), 3.20/t (J=7) 2H (=C-CH$_2$-).

The formation of 2 is rationalized by a stepwise mechanism. Attack of the double bond of 1 on the electrophilic carbon of CSI generates intermediate A which ring-opens[11)] to intermediate B. The last step is ring closure onto oxygen to yield 2. The double bond of 1 is sterically hindered, however strain in the cyclopropyl ring promotes the first two steps[12)]. Exclusive cyclization onto oxygen is surprising for a monoolefin CSI reaction. However, stepwise addition of CSI with charge separation[7)] favors oxygen closure in dienes[6)] and trienes[7,8)] and this may be the explanation for the reaction of 1 with CSI which passes through the dipolar intermediates A and B.

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(10) All new compounds gave satisfactory elemental analysis.

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(12) Diphenylmethylenecyclobutane did not react with CSI at the same conditions.