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REACTION OF N-ACYLSULFILIMINES WITH DIPHENYL KETENE. A NEW SYNTHESIS OF 2-OXAZOLIN-4-ONES

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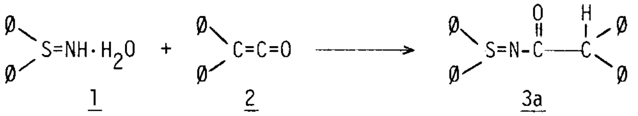
ABSTRACT: 2-Substituted-5,5-diphenyl-2-oxazolin-4-ones[1] are prepared in good to high yields by reaction of diphenyl ketene and N-acylsulfilimes.

Sulfilimines are a class of sulfur-nitrogen ylids which possess both a nucleophilic nitrogen and a good leaving group. Recently, this characteristic has begun to make sulfilimines attractive intermediates for synthesis. Our long interest in the synthesis and chemistry of sulfilimines led us to investigate their reaction with ketenes.

Oae[2a,b] et al. had demonstrated that S,S-diphenylsulfilimine 1 reacts readily with a variety of acylating agents, such as acid chlorides and anhydrides, to afford the corresponding N-acylated sulfilimines. More recently, Tomimatsu[3] and coworkers reported that equimolar amounts of 1 and diphenyl ketene 2 react at 0°; the product is S,S-diphenyl-N-(diphenylacetyl)-sulfilimine 3a, obtained in 34% yield (Eq. 1).


(Eq. 1)

We repeated the reaction of Eq. 1 at 0° and also at room temperature in methylene chloride; the product 3a was obtained in yields of up to 75%. However, when two moles of diphenyl ketene per mole of sulfilimine 1 were employed the yield of 3a became vanishingly small, a surprising result. Compound 3a had apparently reacted with the second mole of ketene with concomitant loss of diphenyl sulfide (isolated and identified), to afford 2-diphenylmethyl-5,5-diphenyl-2-oxazolin-4-one, 4a (mp 166-7° dec) in 73% yield.

In confirmation of the stepwise nature of this reaction sequence, diphenyl ketene was shown to undergo facile addition to 3a at 0°, also yielding 4a.

Diphenyl ketene reacts similarly with other N-acylsulfilimines 3a-d to afford 2-substituted-5,5-diphenyl-2-oxazolin-4-ones 4a-d (Eq. 2) or derivatives thereof (vide infra).[4]

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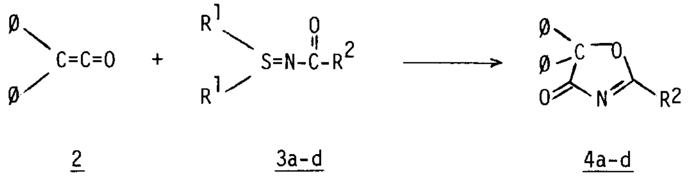


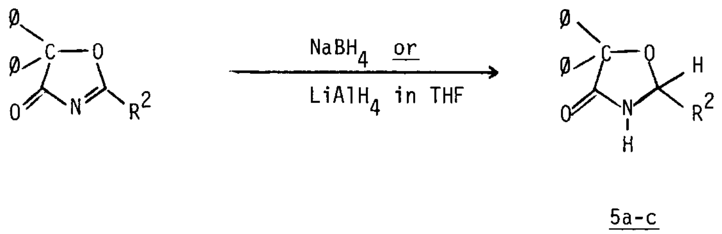
(Eq. 2)

3	R^1	R^2 (3 and 4)
a	-Ph	$-CHPh_2$
b	$-CH_3$	-Ph
c	-Ph	$-CH_3$
d	-Ph	$-CF_3$

When equimolar amounts of S,S-dimethyl-N-benzoylsulfilimine 3b and 2 were refluxed for 4 hours in toluene, 2,5,5-triphenyl-2-oxazolin-4-one 4b (mp 167-8°, lit mp 169°;[5a] 168-70[5b]) was isolated in 80% yield.

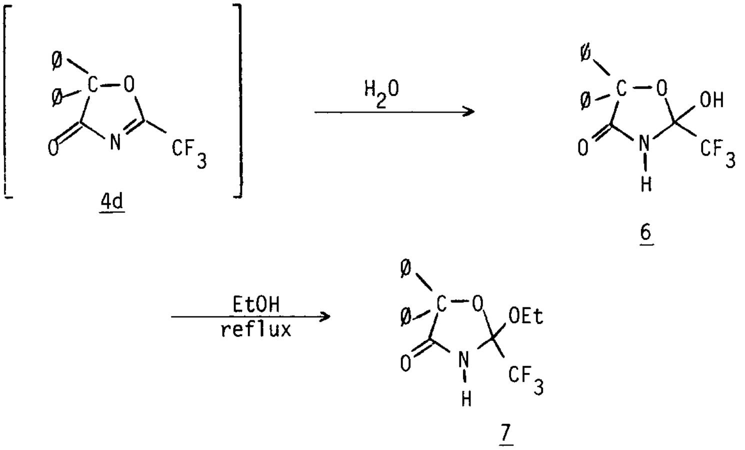
S,S-Diphenyl-N-acetylsulfilimine 3c reacts completely (tlc) with 2 in methylene chloride within 1 hour at room temperature; all attempts to isolate the product initially formed (presumably 2-methyl-5,5-diphenyl-2-oxazolin-4-one, 4c) led to its decomposition, possibly due to the acidity of the hydrogens of the C-2 methyl group. However, removal of the solvent and treatment of the crude residue with excess $NaBH_4$ in i-PrOH led to reduction of the C=N bond; 2-methyl-5,5-diphenyl-4-oxazolidinone 5c (mp 199-200.5°, lit mp 218-19°[6]) was isolated in 56% yield (based on 3c).

$NaBH_4$ and $LiAlH_4$ cleanly and efficiently reduce the 2-oxazolin-4-ones 4a-c to the corresponding 4-oxazolidinones 5a-c[7] (Eq. 3).



(Eq. 3)

S,S-Diphenyl-N-trifluoroacetylsulfilimine 3d[8] reacts slowly with 2 (18 hrs, refluxing xylene) to afford 2-hydroxy-2-trifluoromethyl-5,5-diphenyl-4-oxazolidinone 6 (mp 181-181.5°) in 68% yield. The parent 2-oxazolin-4-one 4d could not be isolated, adventitious moisture rapidly adding to the C-N double bond, reflecting the substantially enhanced electrophilic character at C-2 in 4d. The effect of the trifluoromethyl group on C-2 is further confirmed by the fact that 6 is converted almost quantitatively in five or more hours to 2-ethoxy-2-trifluoromethyl-5,5-diphenyl-4-oxazolidinone 7 (mp 147-9°) in refluxing anhydrous ethanol. This result can be explained by assuming an equilibrium concentration of 4d and subsequent nucleophilic addition of ethanol (Eq. 4).



(Eq. 4)

The scope and limitations of the reaction of sulfilimines and ketenes or ketene precursors is now being investigated.

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4. All new compounds gave correct elemental analyses. Spectra were consistent with the proposed structures.

5. (a) K. Hohenlohe-Oehringen, Montash. Chem., 89, 588 (1958);
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6. G.S. Skinner and J.C. James, J. Org. Chem., 26, 1450 (1961). Note: We repeated Skinner's procedure for 5c using benzilamide, acetaldehyde and hydrogen chloride. The product obtained was identical in all respects to our sample, including its melting point (200°) and mixture melting point.
7. Compound 5a, 75% yield (mp 210-212° dec). Compound 5b, 83% yield (mp 162-164°).
8. Prepared from 1 and trifluoroacetic anhydride according to the procedure of Oae.

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