The Sulfuric Acid Catalyzed Cyclization of *N*-(*trans*-Cinnamyl)-*p*-nitrobenzamide[1]

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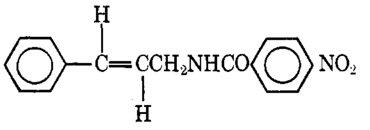
Kashelikar and Fanta[2] reported that treatment of *N*-(*trans*-cinnamyl)-*p*-nitrobenzamide (**1**) with 95% sulfuric acid gave a new compound which was assigned the oxazoline structure **2** solely on the basis of an elemental analysis and the lack of a NH band in the infrared absorption spectrum.



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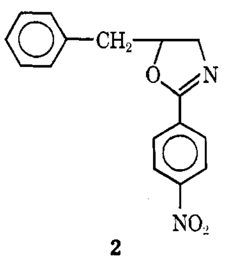

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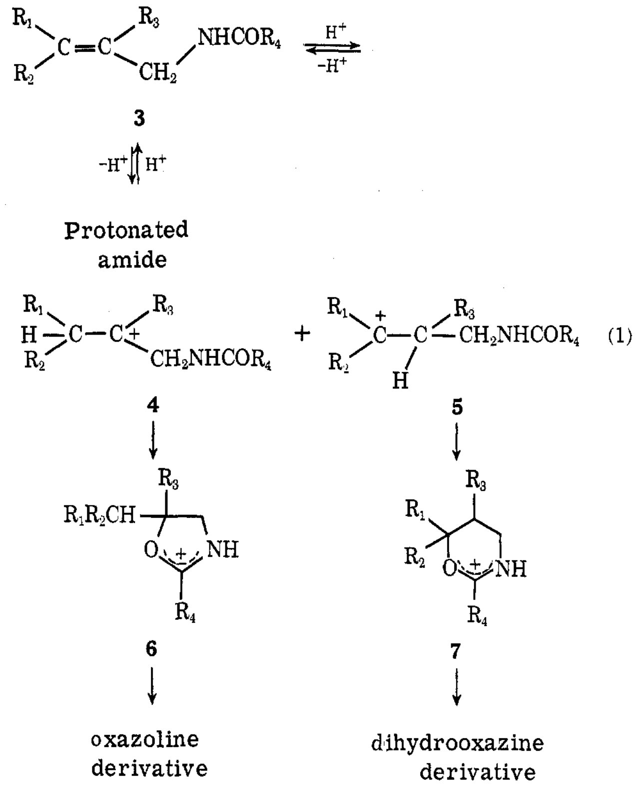
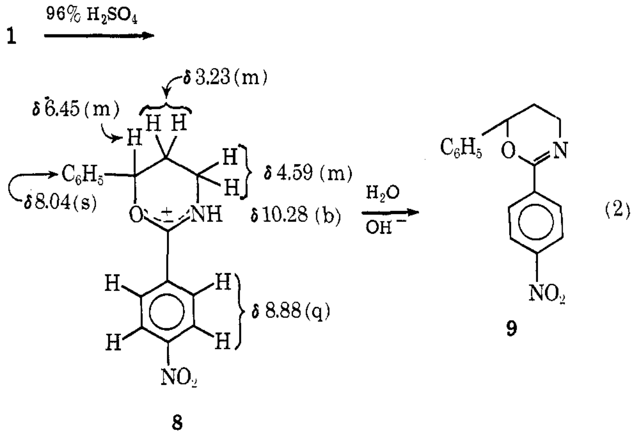
Our recent results[3] suggest that cyclizations of allylic amides in strongly acidic media occur through open carbonium ions (eq 1) instead of proceeding with amide neighboring group participation. Our mechanism would also predict that the major product from such cyclizations would form through the more stable carbonium ion. For example, **3** ($R_1 = R_2 = H$; $R_3 = CH_3$) leads exclusively to **6**, presumably through cation **4**. One would expect that proper substitution for R_1, R_2, and R_3 in **3** could shift the product toward **7** through cation **5**. With R_1 = phenyl and $R_2 = R_3 = H$ in **3**, the expectation of getting **7** (R_1 = phenyl; $R_2 = R_3 = H$) should be realized.

In accordance with this prediction, we found that the nmr spectrum[4] measured after dissolving **1** in 96% sulfuric acid consists of broad multiplets at δ 3.23 (2 protons), 4.59 (2 protons), and 6.45 (1 proton), a sharp singlet at δ 8.04 (5 protons), an A_2B_2 quartet centered at δ 8.88, and a broad peak at δ 10.28 (1 proton). Irradiation of the two-proton multiplet at δ 3.23 caused the spectrum of the proton at δ 6.45 to collapse to a singlet. No other changes in the spectrum occurred. Other than those peaks mentioned, the spectrum was clean. These nmr data fully support the sole formation of the 2-*p*-nitrophenyl-6-phenyl-5,6-dihydro-1,3-oxazinium ion (**8**) in this cyclization reaction (eq 2).





Since rearrangement upon isolation is highly unlikely,[3a] our findings suggest that **1** cyclizes to the oxazine **9** and not to **2** as proposed by Kashelikar and Fanta.[2]

On the basis of these findings, the material prepared more than 12 years ago by Kashelikar,[2] and previously assigned structure **2**, was reexamined. In a capillary melting point tube, it sintered at 112° and melted to a slightly turbid liquid at 113–115°, indicating that only slight decomposition or polymerization had occurred on prolonged standing. A solution of the compound in $CDCl_3$ was filtered to remove a trace of suspended

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[1] (a) Acid-catalyzed Cyclization Reactions. X. For previous papers in the series, see S. P. McManus, J. T. Carroll, and C. U. Pittman, Jr., *J. Org. Chem.*, **35**, 3768 (1970). (b) S. P. M. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

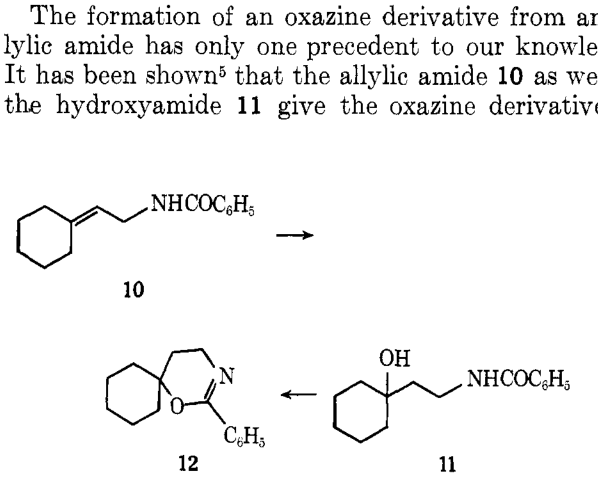
[2] D. V. Kashelikar and P. E. Fanta, *J. Amer. Chem. Soc.*, **82**, 4930 (1960).

[3] (a) See ref 1a; (b) S. P. McManus, B. P. Allen, J. F. Sisson, C. R. Taddei, and C. U. Pittman, Jr., unpublished results.

[4] Nmr spectra were measured in $CDCl_3$ with an internal TMS standard or in sulfuric acid with an external TMS standard (capillary). Either a Varian A-60, HA-100, or Bruker HFX-90 spectrometer was used. All decoupling experiments were performed on the Bruker instrument.

solid and used for the determination of a proton nmr spectrum, which proved to be similar to the spectrum of the oxazinium ion **8**: multiplets at δ 2.15 (2 protons), 3.70 (2 protons), and 5.31 (1 proton), and singlets at δ 7.40 (5 protons) and 8.16 (4 protons). The low-field multiplet was particularly distinctive for structure **9**, and clearly excludes structure **2**.

The formation of an oxazine derivative from an allylic amide has only one precedent to our knowledge. It has been shown[5] that the allylic amide **10** as well as the hydroxyamide **11** give the oxazine derivative **12**



(3)

upon acid-catalyzed cyclization. That example is also good support for our mechanism.[3]

Experimental Section

***N*-(*trans*-Cinnamyl)-*p*-nitrobenzamide (1)**.—Cinnamyl amine, bp 84–87° (1.75 mm), prepared by the procedure of Bottini, *et al.*,[6] was treated with fresh *p*-nitrobenzoyl chloride (0.205 mol, 1:1 ratio with the amine) in the presence of 10 ml of triethylamine with 25 ml of benzene as the solvent. After standing for 10 min, the light yellowish crystals were filtered and washed stepwise with benzene, water, 6 *M* HCl, and water. The amide remaining weighed 2.3 g (85%) and had mp 131–132° (lit.[2] mp 131–132°). The ir and nmr spectra were consistent with the assigned structure (**1**).

2-*p*-Nitrophenyl-6-phenyl-5,6-dihydro-1,3-oxazinium Cation (8).—Amide **1** readily formed **8** upon following the procedure[2] of stirring the amide with sulfuric acid. Alternately, solutions of **8** were formed by extraction of **1** from CCl$_4$ solution. By this method the CCl$_4$ solution of **1** is added dropwise to rapidly stirred H$_2$SO$_4$.

Some attempts to isolate the oxazine **9** from the sulfuric acid solution gave a product which initially had the proper melting point, but rapidly deteriorated to an insoluble, high-melting material which was not further characterized.[7] This deterioration is probably accelerated by traces of acidic or basic impurities.[7]

Registry No.—**1**, 34562-10-2; **2**, 34562-11-3; **8**, 34557-90-9; **9**, 34562-12-4; sulfuric acid, 7664-93-9.

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(5) R. Grewe, H. Pohlmann, and M. Schnorr, *Chem. Ber.*, **84**, 527 (1951).

(6) A. T. Bottini, V. Dev, and J. Klinck, *Org. Syn.*, **43**, 6 (1963).

(7) Since both oxazolines and oxazines readily polymerize, the insoluble matter was probably polymeric; *e.g.*, D. A. Tomalia and D. P. Sheetz, *J. Polym. Sci., Part A*, **4**, 2253 (1966).

2-(*trans*-β-Styrylsulfonyl)- and 2-((*trans*-2-Phenylcyclopropyl)sulfonyl)thiophene

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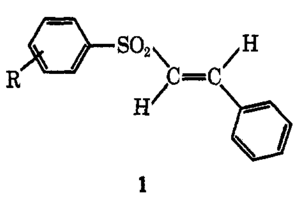
Although *trans*-1-phenyl-2-(arenesulfonyl)ethenes **1**[1,2] and *trans*-1-(arenesulfonyl)-2-phenylcyclopropanes **2**[3,4] are known, the corresponding heterocyclic analogs



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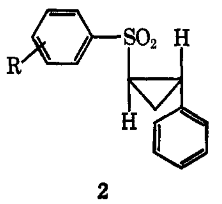

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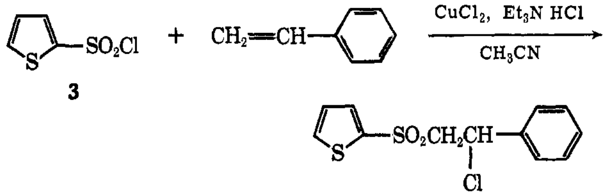
have not been reported. This note reports a facile synthesis of the 2-thiophene derivatives.

The copper-catalyzed addition of arenesulfonyl chlorides to styrenes[2] and other unsaturated substrates[5–7] has recently been described. In the present synthesis, the reaction of 2-thiophenesulfonyl chloride (**3**) with styrene in the presence of cupric chloride afforded 2-((β-chlorophenethyl)sulfonyl)thiophene (**4**, eq 1) in nearly quantitative yield. Subsequent treatment of **4** with triethylamine in benzene gave 2-(*trans*-β-styrylsulfonyl)thiophene (**5**, eq 2).[8] The reaction of **5** with dimethylsulfonium methylide afforded 2-((*trans*-2-phenylcyclopropyl)sulfonyl)thiophene (**6**, eq 3) in 84% yield. The apparent first-order values for



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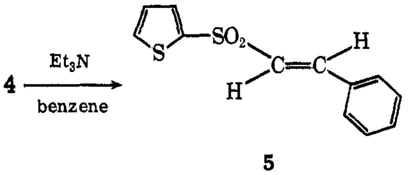

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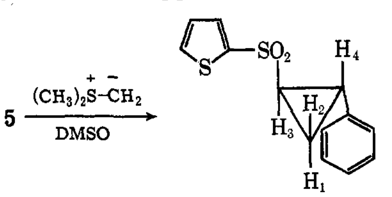

(3)

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(1) V. Baliah and M. Seshapathirao, *J. Org. Chem.*, **24**, 867 (1959).

(2) W. E Truce and C. T. Goralski, *ibid.*, **36**, 2536 (1971).

(3) W. E. Truce and V. V. Badiger, *ibid.*, **29**, 3277 (1964).

(4) W. E. Truce and C. T. Goralski, *ibid.*, **34**, 3324 (1969).

(5) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).

(6) W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J Org. Chem.*, **35**, 4217 (1970).

(7) W. E. Truce and C. T. Goralski, *ibid.*, **35**, 4220 (1970).

(8) The vicinal coupling constant of the vinyl protons is 15.6 Hz, indicating that **5** has the trans configuration.