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PARTIAL ASYMMETRIC PUMMERER REACTION OF ARYL PROP-2-YNYL SULFOXIDE WITH ACETIC ANHYDRIDE

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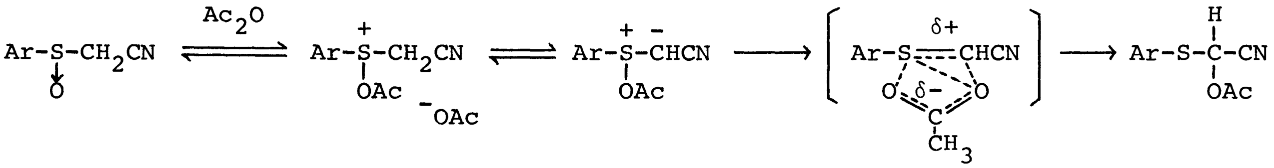
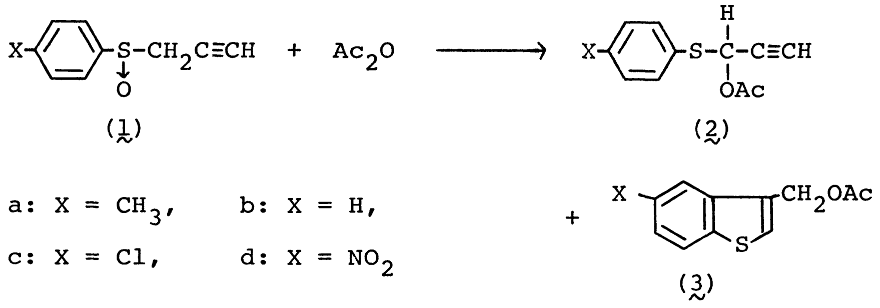
The Pummerer reaction of aryl prop-2-ynyl sulfoxides with acetic anhydride was found to be stereospecific. From the ^{18}O-tracer studies, the asymmetric induction at α-carbon is considered to be caused by an intramolecular and somewhat synchronized 1,2-acetoxy migration within the ylide intermediate.

Recently we reported that the Pummerer reaction of an optically active aryl cyanomethyl sulfoxide with acetic anhydride was stereospecific, inducing a partial asymmetry at α-carbon, and the asymmetric induction was suggested to be caused by an exclusive intramolecular 1,2-acetoxy migration which was confirmed by ^{18}O-tracer experiments.[1)]



In our effort to seek other examples of asymmetric Pummerer reaction, we found that the Pummerer reaction of aryl prop-2-ynyl sulfoxide is partially stereospecific. We now wish to report the stereochemical results together with the data on the ^{18}O-tracer experiments in the Pummerer reaction of aryl prop-2-ynyl sulfoxides.

A few p-substituted aryl prop-2-ynyl sulfoxides (1) were prepared and heated with a large excess of acetic anhydride at 60-90°C for 4-48 hrs. After evaporation of excess Ac_2O and any volatile product in vacuo, the products obtained were separated by column chromatography with silica-gel using benzene-hexane as the eluent to afford the corresponding Pummerer product, 1-acetoxyprop-2-ynyl aryl sulfide(2), in 15-83% yields. There was a concomitant formation of 3-acetoxymethyl 5-substituted benzo[b]thiophene (**3**)[2] (see Table).



(**1**) (**2**) (**3**)

a: X = CH_3, b: X = H,

c: X = Cl, d: X = NO_2

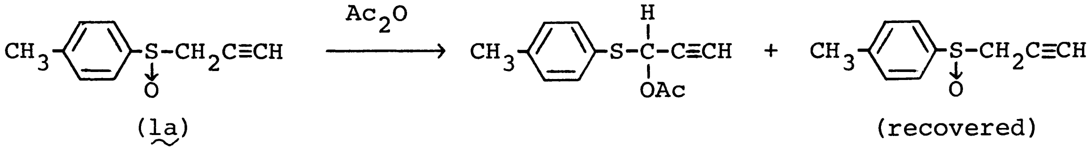
Table

Reaction of aryl prop-2-ynyl sulfoxide(**1**) with acetic anhydride

Sulfoxide(**1**)	Reaction Temp. (°C)	Reaction Time (hr)	Yields (%) (**2**)	Yields (%) (**3**)
1a	60	10	83	trace
	90	2	57	22
1b	60	24	75	16
	90	4	50	39
1c	60	24	69	17
1d	60	48	15	65

Since the Pummerer reaction occurred predominantly in the reaction of prop-2-ynyl p-tolyl sulfoxide (**1a**) with Ac_2O at 60°C, both optically active and ^{18}O-labeled prop-2-ynyl p-tolyl sulfoxides (**1a**) were synthesized and treated with acetic anhydride.

When the optically active sulfoxide [(+)**1a**, $[\alpha]_D$ +122.2°(c=1.3, acetone)] was heated with Ac_2O until 40% conversion (60°C, 3.5 hrs), the Pummerer rearrangement product (**2a**) obtained was found to be optically active ($[\alpha]_D$ +2.2°(c=5.2, acetone)) after a careful separation by column chromatography. Although the Pummerer product has a low optical rotation, the rearrangement is considered to be highly stereo-



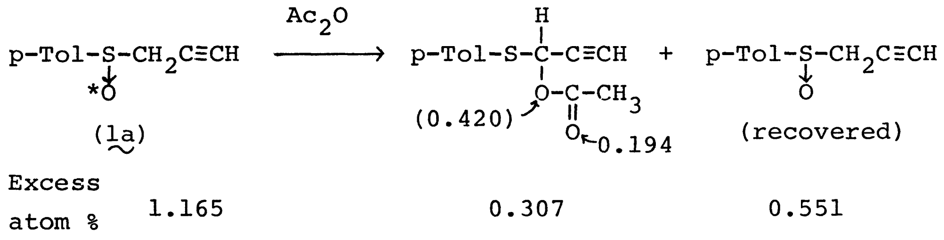
(**1a**) (recovered)

$[\alpha]_D$ +122.2° $[\alpha]_D$ +2.2° $[\alpha]_D$ +11.1°

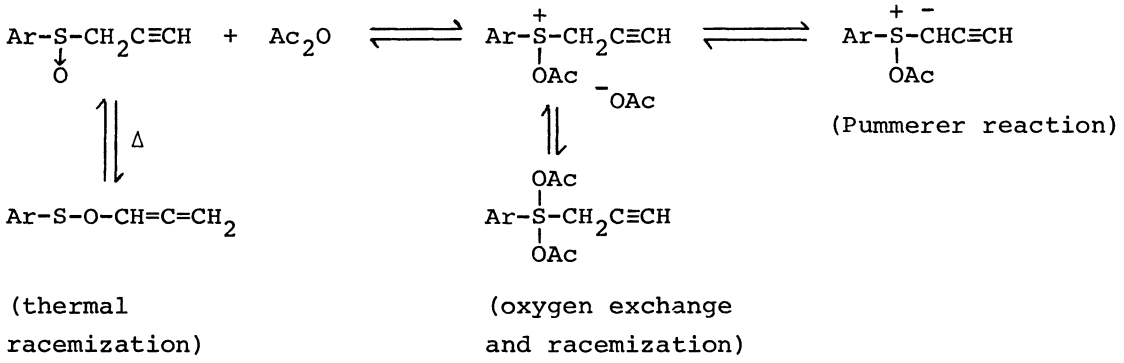
specific in view of the fact that the starting sulfoxide recovered after 40% conversion has only $[\alpha]_D$ +11.1°(c=3.3, acetone)(91% racemization).[4]

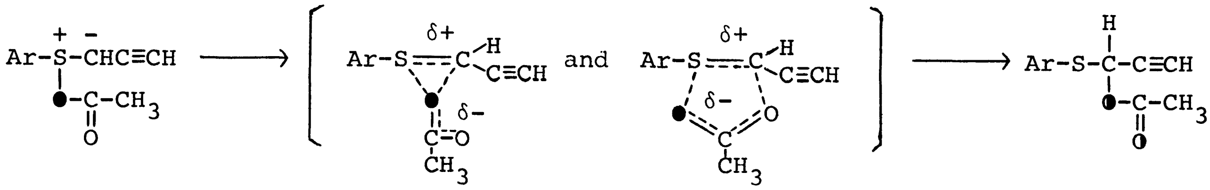
When ^{18}O-labeled prop-2-ynyl sulfoxide (1a) [1.165 excess atom %] was allowed to react with a large excess of acetic anhydride until 40% conversion (60°C, 3.5 hrs), and the original sulfoxide recovered and the Pummerer product separated were subjected to the routine ^{18}O-analysis, the Pummerer product (2a) was incorporated by 53% of ^{18}O [0.307 ex. atom %] based on the starting sulfoxide, while the recovered sulfoxide retained only 47% ^{18}O-content [0.551 ex. atom %] based on the starting sulfoxide. Thus this Pummerer reaction proceeds through an intramolecular 1,2-acetoxy migration at least 53%. However, when one considers the facile oxygen exchange of the starting sulfoxide with acetic anhydride in the Pummerer reaction conditions, the actual intramolecular 1,2-acetoxy migration in the Pummerer reaction should be more than that observed.

In order to understand the mode of migration, the distribution of ^{18}O in both oxygens in the ester function was determined by treatment with 2 molar excess phenylhydrazine. Acetyl in the ester was then converted to 1-acetyl-2-phenylhydrazine [0.194 ex. atom %]. The following uneven ^{18}O distribution in the ester was observed, in keeping with the intramolecular nature of the rearrangement.



These observations suggest strongly that the Pummerer reaction leading to the asymmetric induction may be illustrated as shown below.





(sliding mode) (cyclic mode)

Major Minor

The intramolecular and somewhat synchronized 1,2-acetoxy migration via 3-membered (sliding mode) and 5-membered (cyclic mode) cyclic routes within the ylide molecule is considered to be mainly responsible for the asymmetric induction.

References and Notes

1. T. Numata and S. Oae, Tetrahedron Lett., 1337 (1977), and related references cited therein.
2. The nmr, ir and mass spectra of the benzo[b]thiophene derivative (**3d**) were consistent with those of the authentic sample synthesized by the reaction of aryl prop-2-ynyl sulfoxide (**1d**) with acetic acid at 90°C (35% yield) according to the reported procedure.[3]
3. Makisumi and Takada reported that aryl prop-2-ynyl sulfoxide is transformed by heating at 80°C in nucleophilic solvent, such as AcOH, PhSH, EtOH and H_2O, to 3-(substitutedmethyl)-benzo[b]thiophene derivative which would be formed through an initial thermal transformation to allenic sulfenate, followed by a thermal thio-Claisen type rearrangement [Y. Makisumi and S. Takada, J. Chem. Soc., Chem. Commun., 848 (1974)].
4. Racemization of sulfoxide would be derived from both thermal [2,3]-sigmatropic sulfoxide – sulfenate equilibrium[5] and oxygen exchange reaction of sulfoxide with acetic anhydride.
5. M. Cinquini, S. Colonna, F. Cozzi, and C.J.M. Stirling, J. Chem. Soc., Perkin I, 2061 (1976).

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