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TANDEM [2,3]SIGMATROPIC REARRANGEMENT OF A SULPHONIUM YLIDE AND CYCLOPROPANATION OF THE RESULTING ELECTRON-RICH OLEFIN ON A 4-METHOXY-2-PYRONE DERIVATIVE

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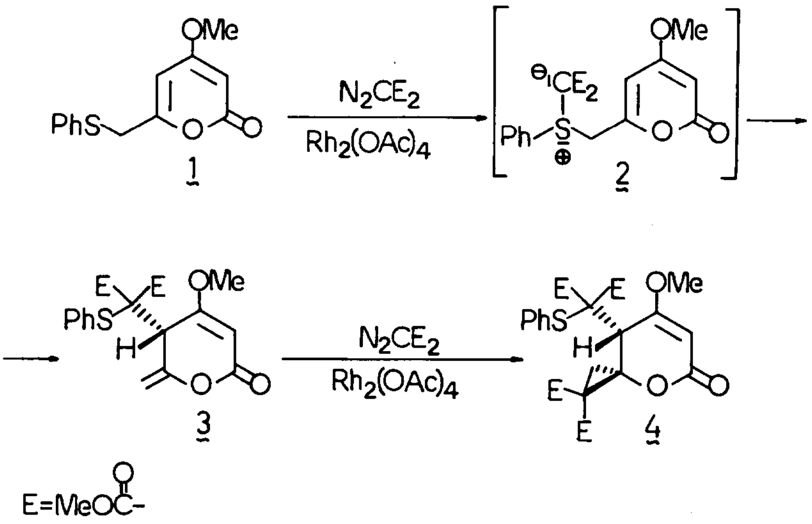
Summary: Rhodium catalyzed reaction of 4-methoxy-6-phenylthiomethyl-2-pyrone with dimethyldiazomalonate affords 5-(bis(methoxycarbonyl))(phenylthio)methyl-4-methoxy-6-methylene-5,6-dihydro-2-pyrone via [2,3]sigmatropic rearrangement of the corresponding sulphur ylide. Cyclopropanation of the 6-methylene double bond occurs by the less hindered side.

It is well known that sulphur ylides are formed by the addition of carbenes or carbenoid species, usually generated from diazocompounds, to sulphides. Allylic sulphonium ylides undergo [2,3]sigmatropic rearrangements, the so called Sommelet-Hauser rearrangement[1].

On the other hand, many natural δ-pyrones have alkyl groups at C-5, no general method to introduce them at this position being available. However, we have recently reported preliminary results on the functionalization of the C-5 position of triacetic acid lactone (4-hydroxy-6-methyl-2-pyrone) derivatives by means of [2,3]sigmatropic rearrangements of sulphonium ylides[2].

On extending the scope of the method, we have found that when 4-methoxy-6-phenylthiomethyl-2-pyrone, **1**,[2] was treated in toluene at 90°C with two equivalents of dimethyldiazomalonate in the presence of rhodium acetate catalyst, two products were isolated. The minor product was identified as 5-(bis(methoxycarbonyl))(phenylthio)methyl-4-methoxy-6-methylene-5,6-dihydro-2-pyrone, **3**, (17%; mp 124-5°C; PMR ($CDCl_3$) δ 3.56 (s, 3H), 3.58 (s, 3H), 3.76 (s, 3H), 4.31 (s, 1H), 4.84 (d, J=2.5 Hz, 1H), 5.05 (d, J=2.5 Hz, 1H), 5.33 (s, 1H), 7.20-7.67 (m, 5H); MS (*m/z*) 378 (M^+, 13%))[3]. This product arises directly from the [2,3]sigmatropic rearrangement of the sulphonium ylide **2**. It is noteworthy that the exocyclic double bond of **3** does not isomerize to afford the fully conjugated pyrone.

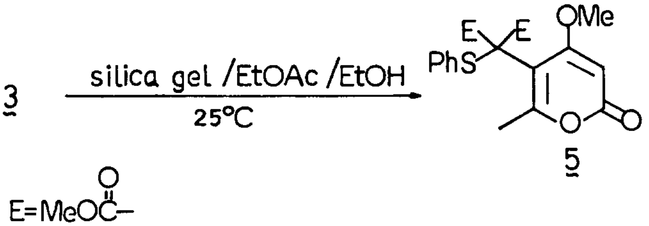
The main product of the reaction arises from the participation of two equivalents of diazomalonate (53%; mp 139-40°C; PMR ($CDCl_3$) δ 2.14 (d, J=7 Hz, 1H), 2.28 (d, J=7 Hz, 1H), 3.47 (s, 3H), 3.65 (s, 3H), 3.69 (s, 3H), 3.75 (s, 3H), 3.81 (s, 3H), 4.48 (s, 1H), 5.36 (s, 1H), 7.19-7.72 (m, 5H); MS (*m/z*) 508 (M^+,2.3%)); molecular formula $C_{23}H_{24}O_{11}S$)[3]. An X-ray diffraction analysis unambiguously proved the structure to be (5*SR*, 6*SR*)-4-methoxy-7,7-bis-



(methoxycarbonyl)-5-(bis(methoxycarbonyl))(phenylthio)methyl-1-oxaspiro[5.2]oct-3-en-2-one, **4**. This compound results from the carbene or carbenoid addition to the exocyclic double bond of **3** by the less hindered side. The electron-rich olefin attacks the electrophilic bis(methoxycarbonyl)carbene.

To the best of our knowledge this is the first example of a [2,3]sigmatropic rearrangement of a sulphur ylide followed by the cyclopropanation of the resulting double bond.

When the reaction was carried out using a 1.0:1.2 ratio of **1** to diazoderivative, compound **3** was isolated in 89% yield, and the presence of **4** was reduced to only 8%. This is the highest yield ever achieved in a functionalization of the C-5 position on a triacetic acid lactone derivative. The conjugate lactone 4-methoxy-5-(bis(methoxycarbonyl))(phenylthio)-methyl-6-methyl-2-pyrone, **5**, (mp 116-8°C; PMR ($CDCl_3$) δ 1.87 (s, 3H), 3.50 (s, 3H), 3.78 (s, 6H), 5.25 (s, 1H), 7.0-7.6 (m, 5H); MS (*m/z*) 378 (M^+, 1.9%)) was prepared in 76% yield by isomerization of **3**.



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References and Notes

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2.- P.de March, M. Moreno-Mañas and I. Ripoll, Synth. Commun., 14, 521 (1984).
3.- All new compounds gave correct elemental analysis.

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