

CYCLISATION REACTIONS OF ALKENYL β -KETOESTERS INVOLVING A NOVEL PHENYLSELENO GROUP MIGRATION

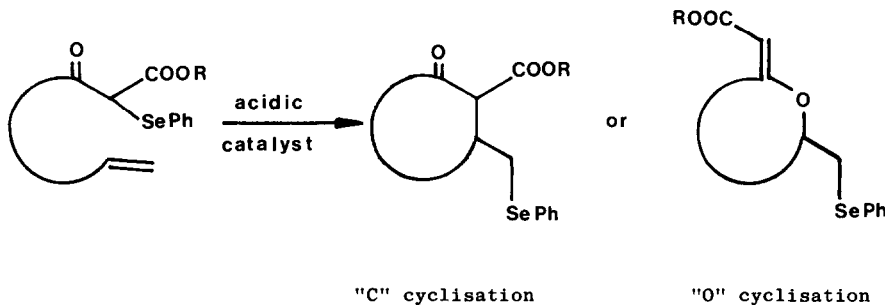
William P. Jackson, Steven V. Ley*, and Judith A. Morton.

Department of Chemistry, Imperial College, London SW7 2AY.

SUMMARY: A number of alkenyl-substituted α -phenylseleno β -ketoesters can be cyclised in the presence of acidic catalysts in which a novel migration of phenylseleno moiety occurs.

Recently it has been shown that alkenyl-substituted β -dicarbonyl compounds can be cyclised using certain phenylselenating reagents and that the products of the reaction could be varied depending upon the reaction conditions.^{1,2}

Here we show that it is possible to effect similar cyclisation via a rearrangement of alkenyl-substituted α -phenylseleno β -ketoesters in the presence of acidic catalysts as in the scheme below.

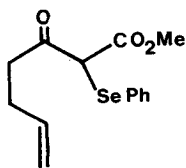


The starting phenylseleno alkenyl β -ketoesters³ (1) + (8) were readily prepared by quenching the anions of the corresponding alkenyl β -ketoesters with N-phenylselenophthalimide.⁴ Upon treatment with various catalysts, at room temperature in CH_2Cl_2 , (1) + (8) gave the cyclised products⁴ in reasonable yields (Table). From the Table it is clear that, in most cases, one can selectively achieve cyclisation via either the central carbon atom of the β -ketoester unit

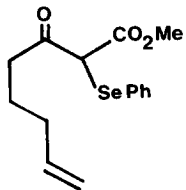
(C-cyclisation) or via the enolic oxygen atom (O-cyclisation). In general, O-cyclisation is achieved with p-toluenesulphonic acid as catalyst or if the reaction is worked up after a short period of time (kinetic product). C-cyclisation is favoured if strong Lewis acids (e.g. SnCl_4) are used and the reaction performed for longer periods of time (thermodynamic product).

TABLE - Reaction of Phenylseleno Alkenyl β -Ketoesters
with Acid Catalysts

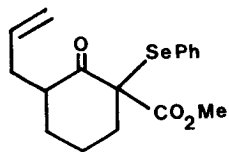
Starting Material	Catalyst (equiv.)	Time	Product ³	%Yield
(1)	SnCl_4 (0.35)	1.7 h	(9)	77
	PTSA (trace)	1.7 h	(10)	52
(2)	SnCl_4 (0.5)	2 h	(11)	67
(3)	SnCl_4 (1.0)	17 h	(12)	88
	SnCl_4 (0.1)	5 min	(13)	80
(4)	SnCl_4 (0.075)	15 min	(14)	79
(5)	SnCl_4 (0.5)	5 min	(15)	62
	PTSA (trace)	5 min	(16)	87
(6)	SnCl_4 (0.5)	25 min	(17)	55
(7)	SnCl_4 (0.5)	30 min	(18)	30
(8)	SnCl_4 (0.5)	5 min	(19)	84
	ZnI_2 (1.1)	5 h	(20)	55



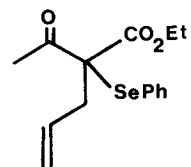
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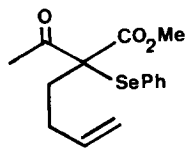
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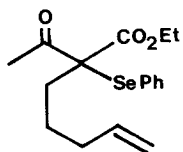
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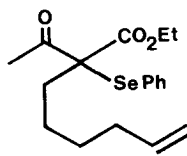
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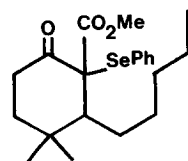
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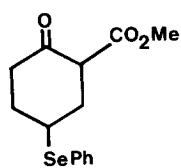
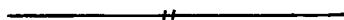
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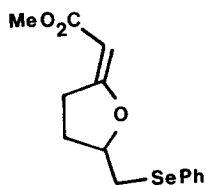
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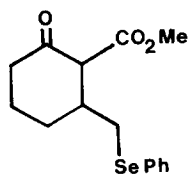
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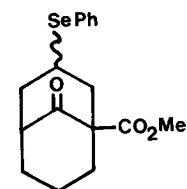
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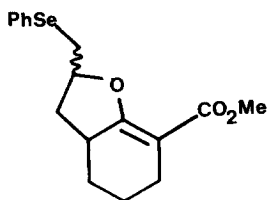
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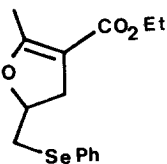
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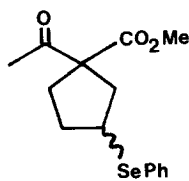
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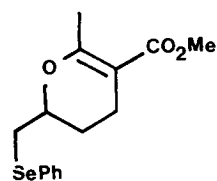
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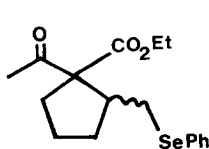
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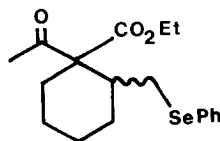
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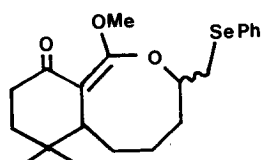
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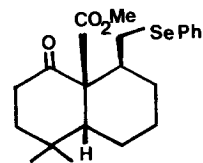
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The low yield of cyclised product from (7), using SnCl_4 , was due to competitive dephenylselenation and to the formation of a product arising from addition of phenylselenenyl chloride to the alkene bond of this deselenated material.

During the cyclisation of (8) we observed the formation of the O-cyclised product (19) after brief treatment with Lewis acids, however, owing to its instability towards t.l.c., this material (19) (ν_{max} 1650, 1610, 1575 cm^{-1} ; δ 0.91 (3H, s), 0.96 (3H, s), 1.17-2.35 (11H, m), 3.0-3.4 (2H, m), 3.77 (3H, s), 3.7-4.0 (1H, m), and 7.0-7.5 (5H, m)) could never be obtained in \geq 90% purity. Prolonged treatment of (8) with the Lewis acid readily afforded the C-cyclised compound (20).

Further examples of these novel rearrangements together with their application to natural product synthesis will be reported later.

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REFERENCES AND FOOTNOTES

1. W.P. Jackson, S.V. Ley, and J.A. Morton, J. Chem. Soc., Chem. Commun., 1980, 1028.
2. W.P. Jackson, S.V. Ley and A.J. Whittle, J. Chem. Soc., Chem. Commun., 1980, 1173.
3. All new compounds were characterised by spectroscopic techniques and accurate mass and/or microanalysis.
4. K.C. Nicolaou, D.A. Claremon, W.E. Barnette and S.P. Seitz, J. Am. Chem. Soc., 1979, 101, 3704.
5. Relative stereochemistries of the functional groups in (20) were assigned after X-ray crystallographic analysis of a later derivative. We thank Dr. D.J. Williams (Imperial College) for this result.

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