New Cyclization Procedure for Alkenyl-substituted β-Dicarbonyl Compounds using *N*-Phenylselenophthalimide

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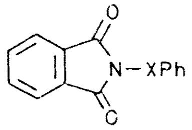
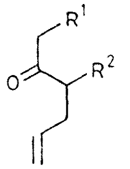
Summary *N*-Phenylselenophthalimide can be used as an effective cyclizing reagent for certain alkenyl-substituted β-dicarbonyl compounds to give a number of polyfunctionalised products.

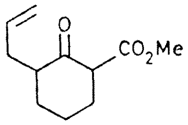
N-PHENYLTHIOPHTHALIMIDE[1] (**1**) and more recently *N*-phenylselenophthalimide[2] (**2**) have been shown to be useful reagents for effecting a variety of synthetic transformations. Here we discuss the use of (**2**) as a suitable cyclizing reagent for certain alkenyl-substituted β-dicarbonyl compounds (**3**)—(**7**). At room temperature, with CH_2Cl_2 as solvent, the compounds (**3**)—(**7**) were treated with (**2**) under different catalytic conditions and, on work-up, gave the cyclized products (**8**), (**10**), (**12**), (**13**), (**15**), and (**16**) (Table). In most cases, cyclization took place *via* the oxygen atom of the enolic form of the dicarbonyl system with a presumed intermediate seleniranium ion. While seleno-moderated cyclizations involving alcohols and phenols are known,[3] the present work constitutes the first examples of reaction of alkenyl-substituted β-dicarbonyl species.



(1) X = S
(2) X = Se



(3) R^1 = H, R^2 = CO$_2$Et
(4) R^1 = CO$_2$Et, R^2 = H



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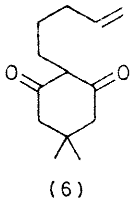

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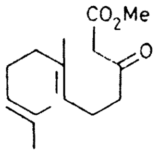

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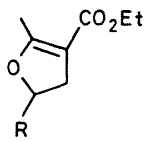
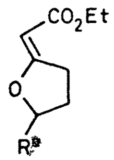
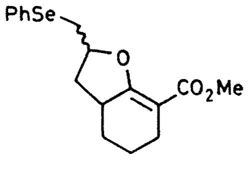


(8) R = CH$_2$SePH
(9) R = Me



(10) R=CH$_2$SePh
(11) R=Me



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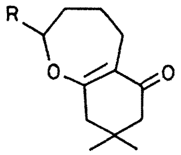
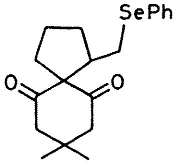


(13) R=CH$_2$SePh
(14) R=Me



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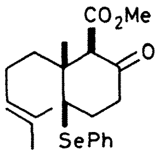

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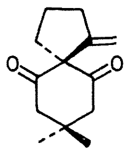

(17)

The cyclized products were fully characterised by the usual methods (^{1}H n.m.r., i.r., acc. mass, and/or microanalysis) and in certain cases were additionally characterised by reduction of the phenylseleno-group with triphenyltin hydride (Table).[4]

Interestingly, when the pentenyl-substituted dimedone compound (**6**) was treated with (**2**) in the presence of a catalytic amount of iodine the oxygen-cyclized product (**13**) was obtained. However, under acidic conditions both the

TABLE. Reaction of β-dicarbonyl compounds with 1·1 equiv. of *N*-phenylselenophthalimide in CH_2Cl_2.

Substrate	Product (% yield) I_2[a]	 p-MeC$_6$H$_4$SO$_3$H[a]	 ZnI_2[b]	Reduced product[e] (% yield)
(**3**)	(**8**) (76)	(**8**) (80)	(**8**) (81)	(**9**) (92)
(**4**)	(**10**) (61)	(**10**) (68)	(**10**) (82)[c]	(**11**) (91)
(**5**)	(**12**) (33)	(**12**) (66)	(**12**) (44)	—
(**6**)	(**13**) (56)	(**13**) (49)	—	(**14**) (91)
	—	(**15**) (42)	(**15**) (66)	—
(**7**)	—[d]	—[d]	(**16**) (67)	—

[a] 0·05 Equiv. of catalyst. [b] 1 Equiv. of catalyst. [c] Tetrahydrofuran as solvent. [d] Complex reaction mixtures. [e] Ph_3SnH (3 equiv.), heat, toluene, azobis-isobutyronitrile.

oxygen- and carbon-cyclized products (**13**) and (**15**) were produced, while in the presence of ZnI_2, (**15**) appeared to be the only product. The reasons for these changes in the reaction pathway are not yet fully understood. Compound (**16**) can also be converted into the known methylene derivative (**17**)[5] in 72% yield by treatment with *m*-chloroperbenzoic acid followed by *syn* elimination of the intermediate selenoxide. It should be noted that an attempted biomimetic cyclization of (**7**)[6] to afford decalins failed and that only during the ZnI_2-catalysed reaction did cyclization *via* carbon take place, giving (**16**) as the major product.

The above cyclization procedure can be compared with other literature methods which give similar compounds,[7] although the incorporation of the highly flexible phenylseleno-group[8] into the product could provide distinct synthetic advantages.

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