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Phenylselenoazidation of Conjugated Enals. Allylic Rearrangement of 2-Alkylidene-3-azidopropanals and Propionic Acids

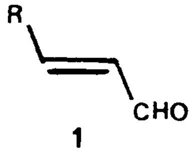
Jean-François HUOT, Francis OUTURQUIN, and Claude PAULMIER*
Laboratoire de Synthèse de Composés thio- et séléno-organiques
(I.R.C.O.F.), UFR Sciences, B.P. 118, Université de ROUEN,
F- 76134 Mont Saint Aignan Cedex, France

β-Azido α-phenylseleno aldehydes were isolated as adducts of $PhSeN_3$ on conjugated enals bearing an α-alkyl substituent. Their oxidation leads to 2-alkylidene-3-azido propanals and propionic acids. An allylic rearrangement of the azido group was observed.

In the preceeding letter,1) we described the preparation of β-methoxy- β-hydroxy- and β-acetoxy-α-phenylseleno aldehydes by the reaction of conjugated enals involving the corresponding oxygen nucleophiles and an intermediate seleniranium cation resulting from the addition of PhSeCl across the C=C bond.

We were interested in analogous reactions using nitrogen nucleophiles. Previous studies deal with the phenylseleno-activated introduction of the nitrite anion on olefins,2) conjugated dienes3) and with that of the azide anion on simple olefins.4-6) It must also be noted that selenenamides add to Michael acceptors like conjugated ketones7) and enals.8)

We present, here, our first results concerning the addition of $PhSeN_3$ on the enals 2 in dimethylsulfoxide 9)and some oxidative and reductive transformations of the adducts.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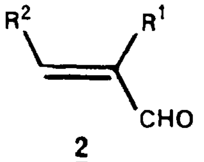
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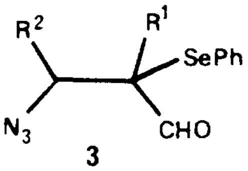
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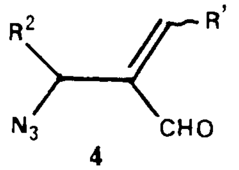
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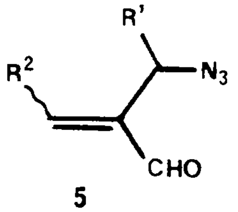
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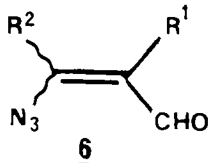
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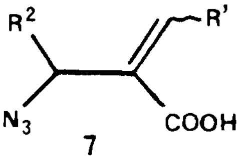
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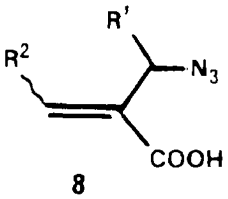
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We first observed that enals 1 which bear no substituent on the α-carbon give complex mixtures probably containing elimination products of the two regioisomeric adducts.[10] With enals 2, the addition products 3 were only formed as mixtures of diastereoisomers. From this result, we can suggest, as previously assumed in the case of oxygen nucleophiles,[1] that the reactions involve the reversible formation of an intermediate seleniranium cation. The oily β-azido aldehydes 3 were readily prepared in very good yields (Table 1).

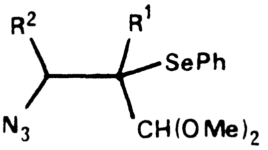
Table 1.[11] β-Azido-α-phenylseleno aldehydes 3 and their oxidation products 4, 5, 6, 7, and 8

No.	R^1 (CH_2R')	R^2	3			Isomer distrib.				Isomer distrib.	
			Yield %	Diast. comp.	Yield %	4	5	6	Yield %	7	8
a	Me	H	91	-	58	50		50	85		
b	Me	Me	90	62/38	60	10	90				
c	Me	Et	80	55/45	62	10	90		90	50	50
d	Me	Ph	93	58/42	85		80	20	75	67	33
e	Et	Me	82	70/30	65	100			62		
f	$-(CH_2)_4-$		79	70/30	52	100			90		

The sodium periodate oxidation of the β-azido-α-phenylseleno aldehydes 3 was then achieved.[12] After syn-elimination reaction on the intermediate selenoxide, 3a leads to a 1:1 mixture of the allylic azide 4a (5a) and the vinylic azide 6a. This result is identical to those concerning the oxidation of β-phenylseleno azides.[4] The β-phenyl substituted aldehyde 3d gives the vinylic azide 6d and the rearranged allylic azide 5d as major compound. The same oxidation of 3b and 3c gave mixtures of the first formed allylic compounds 4b and 4c, respectively, and the rearranged ones 5b and 5c as major components. In the case of the selenides 3e and 3f, the allylic azides of unique structure 4e (5e) and 4f (5f) were isolated with fair yields. (Table 1). The literature does not describe examples of azide allylic rearrangements on structure having a double bond conjugated with a carbonyl group.[13]

As previously described for other structures,[1,14] the hydrogen peroxide oxidation of the α-phenylseleno aldehydes 3 allow the preparation of the α,β-unsaturated carboxylic acids 7 (8). 7c and 7d rearrange partially into the allylic azides 8c and 8d, respectively, as observed for the corresponding aldehydes (Table 1). No traces of vinylic azides analogous to the enals 6 were found in the reaction mixtures.

To determine the stereochemistry of these unsaturated compounds 4-8, a detailed NMR study is under investigation. At this time, we have not established if the rearranged allylic azides 5 correspond to a formal azidation of the α-alkyl group of the enals 2 with retention of the stereochemistry. With the aim to convert the azides 3 into primary amines and amides, we first protected the aldehyde function. The acetals 9 were prepared in good yields.15) The reduction step was achieved by the Staudinger method16) involving the hydrolysis of an intermediate iminophosphorane.17) The unstable amines 10, also obtained by another way,18) were treated with acetic anhydride in methanol. The acetamides 11 were isolated in correct yields.19)



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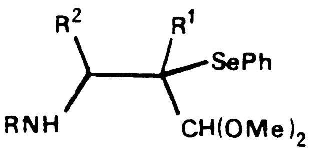
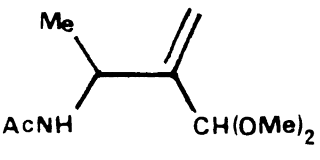


10 R=H 11 R= Ac



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The oxidative syn-elimination process achieved on the amide 11b20) gives the unsaturated acetal 12 in a good yield. Other transformations of structures 10 and 11 leading to α-aminomethyl α,β-unsaturated aldehyde and carboxylic acid derivatives, are now under investigation. The transformations of adducts resulting from the reaction of enals 2 with morpholino benzeneselenenamide is also being studied.8)

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8) J.F. Huot, F. Outurquin, and C. Paulmier, unpublished results.

9) PhSeCl (1.2 equiv.), NaN_3 (1.8 equiv.), DMSO, 20 °C, 16 h.

10) Acetoxyselenenylation of the same enals leads to α-seleno enals (Ref.1).

11) All the compounds isolated were purified by silicagel chromatography and characterized by ^1H and ^{13}C NMR.

12) $NaIO_4$, MeOH, H_2O, $NaHCO_3$, 0 °C → 20 °C, 3 h. The vinylic azides 6a and 6d were separated chromatographically (silicagel, Petroleum ether/CH_2Cl_2 80/20). The allylic azides 4a (5a) and 4c cannot be isolated in pure form.

13) Rearrangements of allylic azides : A. Gagneux, S. Winstein, and W. G. Young, J. Am. Chem.Soc., 82, 5956 (1960) ; C.A. Van Der Werf and V.L. Heasley, J. Org.Chem., 31, 3534 (1966) ; J. Cleophax, A. Olesker, A Rolland,S.D. Gero, and A. Forchioni, Tetrahedron, 33, 1303 (1977) ; I. Z. Kabore, Q. Kuong-Huu, and A. Pancrazi, ibid., 34, 2807 (1978); S.I. Murahashi, Y. Taniguchi, Y. Imada, and Y. Tanigawa, J. Org. Chem., 54, 3292 (1989).

14) H_2O_2 30%, CH_2Cl_2/THF (4/1), - 10 °C → + 20 °C, 16 h. See : F. Outurquin and C. Paulmier, Synthesis, 1989, 689 . The acids 7,8 were purified by basic treatment followed by a careful acidification. They are oily compounds except 7f (8f) : F = 121 °C.

15) MeOH, $HC(OMe)_3$, pTSA, molecular sieves, reflux 4 h. The acetals 9a, 9c, and 9d are oils purified by chromatography and isolated as diastereomeric mixtures : 9a : 69% ; 9c : 77% ; 9d : 64%.

16) PPh_3, THF, reflux 3 h then H_2O. The amines 10 obtained as unstable oils are characterized by ^1H NMR.

17) M. Vaultier, N. Knouzi, and R. Carrie, Tetrahedron Lett., 24, 763 (1983) ; C. Carite, J.P. Alazard, K. Ogino, and C. Thal, ibid., 31, 7011 (1990).

18) $SnCl_2$, PhSH, THF, Et_3N, 20 °C, 0.5 h. See : M. Bartra, P. Romea, F.Urpi, and J. Vilarrasa, Tetrahedron, 46, 587 (1990).

19) Acetamides 11 are oily compounds separated from triphenylphosphine oxide by repeated extractions with warm hexane. Yields : 11b : 62%; 11c : 69% ; 11d : 71%.

20) Compound 12 is prepared (66% yield) by the meta-periodate oxidation of the acetamide 11 (R^1=R^2=Me) (3 h, 20 °C. See Ref.1) and purified by silicagel the chromatography (elution : CH_2Cl_2).

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