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CIS 1,2-FUNCTIONALIZATION OF CYCLOHEXANE USING SELENIUM INTERMEDIATES

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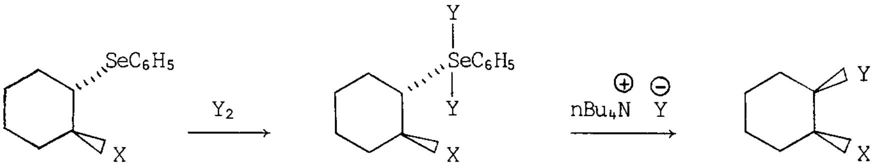
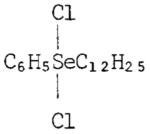
ABSTRACT: The *trans* 1,2-phenylseleno acetate, acetamide, alcohol and nitrile of cyclohexane may be oxidized at selenium by halogens and the phenylseleno moiety displaced by halide to give high yields of 1,2 halide-containing products with *cis* geometry.

Recent work has demonstrated the synthetic utility of organoselenium compounds for the overall *cis* chlorination of alkenes.[1] We now report that a variety of readily available *trans* substituted phenylselenocyclohexanes (1) can be oxidized by either chlorine or bromine to yield the non isolated adducts of structure (2). The phenylseleno moiety of (2) may be displaced by a soluble source of halide (tetra-n-butylammonium halide) under mild conditions to yield *cis* products (3)[2,3] in all cases except one (entries 6,7 Table). This exception is presumably caused by neighbouring group participation which occurs only with chlorine/chloride.

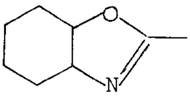


(1) (2) (3)



$C_6H_5SeCl_2C_{12}H_{25}$

(4)



(5)

Generally the dichlorides react more slowly with chloride than the corresponding seleninyl dibromides react with bromide. The dodecylseleninyl dichloride (4) reacts with chloride at room temperature to yield 1-chlorododecane quantitatively. The corresponding dibromide reacts quantitatively and more readily with bromide. The dichloride (4) reacts with bromide to yield a mixture of 1-chlorododecane (60%) and 1-bromododecane (40%).

Table *Preparation of cis 1,2-cyclohexyl halide derivatives*

Entry	Substrate	Reaction Conditions	Product	Yield %
1	(1) X = $OCOCH_3$	Cl_2; Cl^-, R.T., 8h	(3) X = $OCOCH_3$, Y = Cl	82
2	(1) X = $OCOCH_3$	Br_2; Br^-, R.T., 16h	(3) X = $OCOCH_3$, Y = Br	86
3	(1) X = $NHCOCH_3$	Cl_2; R.T., 5h	(3) X = $NHCOCH_3$, Y = Cl (5)	7 87
4	(1) X = $NHCOCH_3$	Cl_2; Cl^-, R.T., 5h	(3) X = $NHCOCH_3$, Y = Cl (5)	62 34
5	(1) X = $NHCOCH_3$	Br_2; Br^-, R.T., 16h	(3) X = $NHCOCH_3$, Y = Br	79
6	(1) X = OH	Cl_2; Cl^-, R.T., 7h	(3) X = OH, Y = Cl 1.5 : 1, *cis : trans*	72
7	(1) X = OH	Cl_2; Cl^-, (10 eq.), R.T., 4h	(3) X = OH, Y = Cl 1.8 : 1, *cis : trans*	74
8	(1) X = OH	Br_2; Br^-, R.T., 3h	(3) X = OH, Y = Br	77
9	(1) X = CN	Cl_2; Cl^-, Δ, 0.75h	(3) X = CN, Y = Cl	92
10	(1) X = CN	Br_2; Br^-, Δ, 0.75h	(3) X = CN, Y = Br	85

REFERENCES

1. A.M. Morella and A.D. Ward, *Tetrahedron Lett.*, *25*, 1197, 1984.

2. *General Procedure.* A solution of chlorine in carbon tetrachloride (2.3 M, 960 μl, 1.1 eq) was added to a cooled solution of *trans*-2-acetoxycyclohexylphenylselenide (594 mg, 2.0 mmol) in dry acetonitrile (10 ml) followed by tetra-n-butylammonium chloride (564 mg, 1 eq). The mixture was stirred at room temperature under nitrogen for 8h, then cooled and oxidized with hydrogen peroxide (28%, 1.0 ml, 5 eq) for 10 min. The mixture was evaporated to a small volume, diluted with sodium bicarbonate (10%, 20 ml) and extracted with carbon tetrachloride (3 x 10 ml). The combined extracts were dried ($MgSO_4$), evaporated and distilled to yield *cis*-2-chlorocyclohexyl acetate (302 mg, 82%) b.p. 100-105°/23 mm.

3. In all cases the decoupled proton n.m.r. spectrum of each product showed a $J_{1,2}$ value in the range 0-3 Hz. The *trans* chloro- and bromoacetates showed $J_{1,2}$ coupling of 8-9 Hz. In most cases chemical shift differences between the two isomers also enabled stereochemistry to be assigned unambiguously. In some cases the geometry was checked by comparison with authentic samples.

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