CLEAVAGE OF CARBON — SELENIUM BOND IN SELENOPHENO[2,3-b]THIOPHENE

V. P. Litvinov, I. P. Konyaeva, and Ya. L. Gol'dfarb

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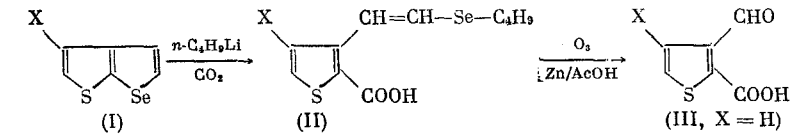
Selenopheno[2,3-b]thiophene (I, X = H) when treated with n-C_4H_9Li, even at −70°, undergoes cleavage at the C−Se bond to give, after carbonation, 3-(β-butylselenoethenyl)thiophene-2-carboxylic acid (II, X = H) in up to 57% yield, mp 90° (from hexane). Found: C 46.14; H 5.14; S 11.17; Se 27.52%. $C_{11}H_{14}O_2SSe$. Calculated: C 45.68; H 4.88; S 11.08; Se 27.30%. m/e 290; NMR spectrum (δ, ppm, $(CD_3)_2CO$): 7.55 (H^4), 7.69 (H^5), 10.47 (COOH), 7.74 and 6.83 (α- and β-protons of −CH=CH−); J_{45} = 5.25 and $J_{-CH=CH-}$ = 11.25 Hz. The ozonolysis of the acid (II, X = H) in CH_2Cl_2 at −78° and subsequent reduction of the products with Zn in AcOH leads to 3-formylthiophene-2-carboxylic acid (III, X = H). The selenophene ring is opened at −70° even when bromine is present in the β-position of (I): from 3-bromoselenopheno[2,3-c]thiophene (I, X = Br) we obtained 4-bromo-3-(β-butylselenoethenyl)thiophene-2-carboxylic acid (II, X = Br) (46%), mp 130-132° (from hexane).



(I) X = H, Br (II) (III, X = H)

The observed selective cleavage of the selenophene ring lacks an analogy in either the selenophene or benzo[b]selenophene series, where the C−Se bond is cleaved to give acetylene derivatives only in the case of the β-lithium-substituted derivatives [1, 2] (cf. [3]). The mechanism of the observed cleavage of the C−Se bond is apparently analogous to that discovered by us previously in the 2-hetarylselenide series [4].

LITERATURE CITED

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