Tetrahedron Letters No. 25, pp 2529 - 2531, 1972. Pergamon Press. Printed in Great Britain.

REACTIONS OF PHENYL VINYL SELENIDE WITH BENZOYL PEROXIDE

Yoshiyuki Okamoto*, Rachid Homsany and Takefumi Yano

Research Division, Department of Chemical Engineering
New York University, University Heights
New York, New York 10453

(Received in USA 13 April 1972; received in UK for publication 15 May 1972)

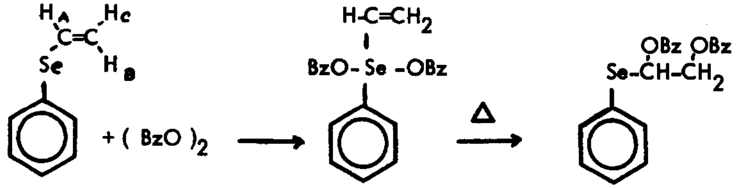
All the attempts to polymerise phenyl vinyl selenide[1] by free radical initiators, such as benzoyl peroxide and azo-bis (isobutyronitrile) in bulk or in benzene, by the sealed tube technique[2], have failed[3]. However, under similar conditions, phenyl vinyl sulphide polymerised readily[4,5].

When phenyl vinyl selenide (I) and benzoyl peroxide (1:1 ratio) solutions in CCl_4 were mixed at room temperature, the colorless solution turned gradually to pale yellow. In a typical reaction, phenyl vinyl selenide (2.00 g, 0.011 mole) in 30 ml of CCl_4 was added dropwise, over 20 min., to a CCl_4 solution (30 ml) of benzoyl peroxide (2.65 g, 0.011 mole). The nmr spectrum of the mixture was recorded as a function of the reaction time. The vinyl protons absorbed at τ 3.36 (proton A, q, J_{AC} 8Hz, J_{AB} 16Hz), 4.43 (proton C, d) and 4.70 (proton B,d). After the mixture was allowed to stand at room temperature, these bands shifted gradually down field to the region of τ 2.7 - 3.7. Several hours later, new bands appeared at τ 5.40. The ir spectrum of the mixture at the initial stage exhibited a broad band at 1650 cm^{-1}. The benzoyl peroxide absorption at 1000, 1760 and 1785 cm^{-1} decreased gradually in intensity.

The solution was refluxed for 2 hours, then CCl_4 evaporated under reduced pressure. The resulting viscous fluid solidified after standing at room temperature for 3 days. The solid was recrystallised from light petroleum ether-benzene, yield 56%, mp. 55°, molecular weight (in benzene); found: 418, Calcd for $C_{22}H_{18}O_4Se$; 425, Anal. Calcd for $C_{22}H_{18}O_4Se$; C: 62.15, H:4.24, Se:18.59. Found: C:61.50, H:4.12, Se:19.22, ir (ν max, CCl_4) 1690 and 1720 cm^{-1} with no appreciable absorptions of the benzoyl peroxide and benzoate anion (1400 and 1600 cm^{-1}), nmr (CCl_4) τ 2.0 - 2.7 (aromatic 15 H, m), 3.43 (1H, q) and 5.46 (2H, t) mass spectrum m/e, 425, 312, 269, 122, 105 and 77.

When the CCl_4 solution of methyl phenyl selenide was added slowly to a solution of benzoyl peroxide in CCl_4 by cooling with cold water, a slight exothermic reaction followed by the precipitation of a white solid was observed. The solid was identified to be methyl phenyl selenium dibenzoate, yield 92%, mp. 116°, molecular weight (in benzene); found: 402, Calcd for $C_{21}H_{18}O_4Se$; 413, Anal. Calcd for $C_{21}H_{18}O_4Se$; C: 61.01 H: 4.36 Se: 19.12, Found: C: 60.75, H: 4.20, Se: 19.85, nmr (CCl_4) τ 7.15 (s, CH_3) vs. 7.80 (s, CH_3) for methyl phenyl selenide; ir (ν max, CCl_4) 1680 and 1725 cm^{-1}.

Thus, the above observation suggested that the reaction of phenyl vinyl selenide with benzoyl peroxide gave phenyl vinyl selenium dibenzoate (II) which subsequently yielded the double bond addition product (III). Attempts to isolate pure II were not successful. A double bond addition product of phenyl vinyl ether with benzoyl peroxide is reported in the literature[6].



(I) (II) (III)

Therefore, the failure of benzoyl peroxide to initiate the polymerisation of phenyl vinyl selenide is attributed to its addition on the selenium atom.

Acknowledgement

The authors gratefully acknowledge the financial support of the Selenium-Tellurium Development Association, Inc.

References

1. Phenyl vinyl selenide was prepared by the reaction of phenyl selenium bromide with magnesium vinyl chloride in THF bp. 60° /3 mm Hg.
2. C. C. Price and J. Zomlefer, J. Amer. Chem.Soc., 72, 14 (1950).
3. Similar observations were reported by H. Kroll and E. F. Bolton in J. Appl. Polym., 14, 2319 (1970).
4. C. C. Price and H. Morita, J. Amer. Chem. Soc., 75, 4747 (1953).
5. K. Tsuda, S. Kobayashi and T. Otsu, J. Polym. Sci., 22, 89 (1968).
6. M.F. Shostakovskii, N.A. Gershtein and V.A. Neterman, Doklady Akad. Nank. S.S.S.R., 103, 265 (1955).