REACTION OF PHENYLBENZOXAZOLE WITH PHENYL GLYCIDYL ETHER

V. V. Korshak, M. A. Surikova,
L. I. Komarova, and N. I. Bekasova

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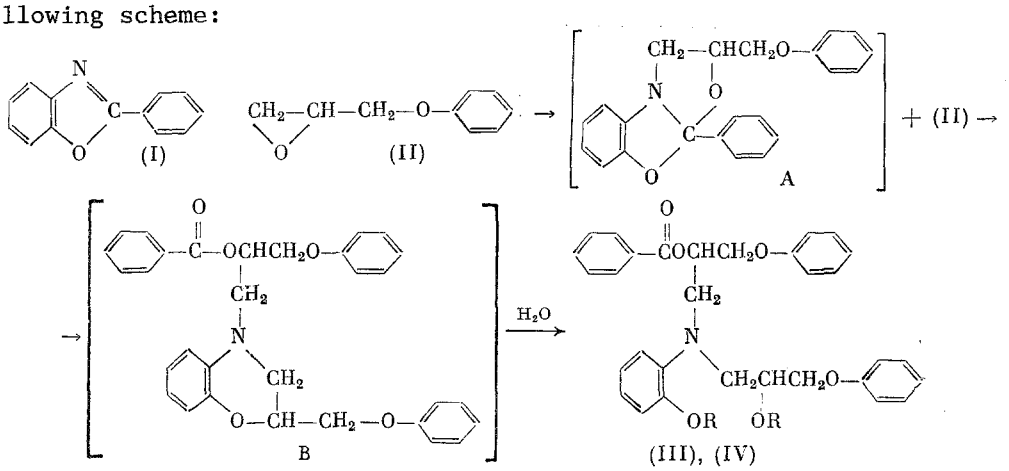
Polyethers, polyamides, and polyimides are used as modifiers for epoxy compounds [1-3]. Starting from epoxy compounds the incorporation of polybenzoxazoles (PBO) gives material with new valuable properties.

Investigation of epoxy compounds with PBO by means of IR spectroscopy showed that PBO is a chemically active modifier. On treatment of the compound a reaction of the α-oxide ring with the benzoxazole ring takes place, which differs from known addition reactions of the oxirane ring to the C=N bond of the heterocycle [4]. On the basis of earlier disclosed facts [5-8] about the insertion of epoxy groups via their opening to molecular chains into a heterobond, such as CO—O, CO—N, and N—CO—N, it may be assumed that the reactions of the α-oxide ring with the benzoxazole ring can also proceed through an insertion reaction.

To determine the course of the reaction and the structures of the compounds produced we have studied the model reaction of phenylbenzoxazole (I) with phenyl glycidyl ether (II). The reaction was carried out at molar ratios of (I) and (II) of 2:1, 1:1, and 1:2 at 180-250°C. Comparison of the IR spectra of the starting mixtures with those obtained after heating them pointed to participation in the reaction of the epoxide (the bands at 3060, 3010, 915, and 865 cm^{-1} disappear) and the benzoxazole rings (sharp reduction of the bands at 930, 1550, and 1620 cm^{-1}). The absorption bands of the aromatic nuclei are retained and intensive absorptions of an ester group of the type Ar—CO—O—Alk appear in the regions 1720, 1270, and 1110 cm^{-1}.

The reaction product containing the ester group has a molecular weight and a composition which correspond with a compound composed of one molecule of (I) and two molecules of (II). This is also confirmed by the quantity of (I) recovered from the reaction mixture because at an equimolar ratio of the reactants, half of (I) is recovered. It is also clear from the IR spectra that the ratio of monosubstituted and 1,2-disubstituted aromatic nuclei in the product obtained is the same as in the mixture in which the ratio of (I) and (II) is 1:2. On the basis of these data it was assumed that the reaction proceeds according to the following scheme:



R = H (III), COPh (IV).

The yield of the resulting reaction product (III) increases when the fraction of (II) in the starting mixture is increased and when the reaction temperature is raised. Thus, the reaction does not proceed below 180°C, the yield of (III) is 10% at 180-200°C, and above

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1356-1359, June, 1987. Original article submitted December 25, 1985.

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230°C side reactions occur. The highest yield of 60% of (III) is obtained at 230°C and a ratio of (I) and (II) of 1:2.

In the IR spectrum of reaction product (III) there is an intensive absorption of OH groups (3350 cm^{-1}), and in the PMR spectrum of (III) a series of multiplets of CH_2 and CH groups are present in the region of 2.5-4.2 ppm. The protons of the benzene rings give multiplets in the region 6.5-7.5 ppm. The ratio of the integrated signals of the aromatic and aliphatic protons is 19:12, that is it corresponds with structure (III) if we assume that the signals of the protons of the OH groups contribute to the multiplet pattern of the aliphatic protons.

The structure of (III) is also confirmed by the preparation of its dibenzoyl derivative (IV), the structure of which has been proved by elemental analysis, the determination of the molecular weight, and the IR spectrum. In the IR spectrum of (IV) there are a number of bands resulting from the vibrations of the ester bonds: in the region of the C=O valence vibrations there are bands at 1724 and 1787 cm^{-1}, corresponding with two types of ester groups, Ar—COO—Alk and Ar—COO—Ar. The absorption band of the OH groups at 3350 cm^{-1}, which is present in the IR spectrum of (III), is lacking in the spectrum of product (IV).

On the basis of literature data [4] we may assume that the initial step of the reaction is the addition of the oxirane ring to the C=N bond of the heterocycle with the formation of intermediate A. A second molecule of (II) is added to intermediate A, inserting into the $\rangle N—C—$ bond in which the C atom is linked to two O atoms, as a result of which product B is formed. This assumption is based upon known facts about the course of insertion reactions at polar heterobonds of similar types: the amide C—N, ester C—O, N—Si, and Si—O bonds [6, 7, 9].

The proposed scheme suggests opening of the α-oxide ring at the terminal carbon atom (in much the same way as the data of [10]), although opening of the oxirane ring at the β-carbon atom is not excluded.

EXPERIMENTAL

IR spectra were recorded from films on Perkin-Elmer-457 and UR-20 spectrophotometers, and PMR spectra on a Perkin-Elmer R-12 (60 MHz) instrument from 20% solutions in trichloroethane with HMDS as standard. TLC was carried out on Silufol UV-254 in CH_2Cl_2.

Phenylbenzoxazole (I) was prepared according to [11]. Yield 60%, mp 101.5-102°C.

Phenyl glycidyl ether (II), bp 80-81.5°C/2mm (cf. [12]).

N-(2-hydroxy-3-phenoxypropyl)-N-(2-benzoyloxy-3-phenoxypropyl)-o-hydroxyaniline (III). The synthesis was carried out in glass ampuls under an Ar atmosphere for 6-8 h at 180, 200, 230, and 250°C, at ratios of the starting compounds (I) and (II) of 2:1, 1:1, and 1:2 in the presence of the catalyst PhCOONa (3% of (I)). The mixture was extracted with hexane, the residue was filtered over an SiO_2 column and eluted with CH_2Cl_2; (III) was isolated as a viscous oil. Molecular weight of (III) (ebullioscopy in acetone) 493 (calculated 513), R_f 0.45. Found %: C 72.01, H 6.40, N 2.49. $C_{31}H_{31}NO_6$. Calculated %: C 72.49, H 6.08, N 2.72.

N-(2-benzoyloxy-3-phenoxypropyl)-N-(2-benozyloxy-3-phenoxypropyl)-o-benzoyloxyaniline (IV) was prepared according to [13]. Light-yellow oil. Found %: C 75.02, H 4.90, N 1.84. $C_{45}H_{39}NO_8$. Calculated %: C 74.88, H 5.44, N 1.94. Molecular weight (ultracentrifugation in THF) 741, calculated 721.8.

CONCLUSIONS

The reaction of phenylbenzoxazole with phenyl glycidyl ether is not limited to the addition of the α-oxide ring to the C=N bond of phenylbenzoxazole, but is followed by addition of a second molecule of phenyl glycidyl ether with the formation of an N derivative of hydroxyaniline.

LITERATURE CITED

1. A. M. Paken, Epoxy Compounds and Epoxy Resins [in Russian], Goskhimizdat, Leningrad (1962).

2. A. Noshay and I. M. Robson, J. Pol. Sci., Polym. Chem. Ed., 12, 689 (1974).
3. V. V. Korshak, S. V. Vinogradova, G. L. Slonimskii, et al., Author's Cert. 526641 (1974); Byull. Izobret., No. 32 (1976).
4. H. C. Van der Plas, Ring Transformations of Heterocycles, Vol. 1, Academic Press, New York (1973), p. 28.
5. L. I. Komarova, S. N. Salazkin, V. V. Korshak, et al., Vysokomol. Soedin. 16B, 718 (1974).
6. L. I. Komarova, S. N. Salazkin, M. I. Malaniya, et al., J. Pol. Sci. Polym. Chem. Ed., 16, 1643 (1978).
7. L. I. Komarova, I. A. Bulgakova, S. N. Salazkin, et al., J. Pol. Sci., Polym. Lett. Ed., 14B, 179 (1976).
8. V. V. Korshak, L. I. Komarova, S. V. Vinogradova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1645 (1981).
9. G. S. Bondarevskii, L. I. Komarova, A. I. Kalachev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 454 (1978).
10. G. V. Gridunova, V. E. Shklover, Yu. T. Struchkov, et al., Khim. Geterotsikl. Soedin., 1026 (1984).
11. L. C. Galatis, J. Am. Chem. Soc., 70, 1967 (1948).
12. Y. Tanaka and H. Kakiuchi, J. Polym. Sci. Part A-1, 4, 110 (1966).
13. Organicum, Practical Organic Chemistry [in Russian], Vol. 2, Mir, Moscow (1979), p. 82.

ASYMMETRIC SYNTHESIS BY CATALYTIC REDUCTIVE AMINOLYSIS OF p-FLUORO-α-ACETAMINOCINNAMIC ACID AZALACTONE. COMMUNICATION 18. PREPARATION OF S-(−)-p-FLUOROPHENYLALANINE

L. F. Godunova, E. I. Karpeiskaya, E. S. Levitina, E. I. Klabunovskii, Yu. L. Yagupol'skii, and M. T. Kolycheva

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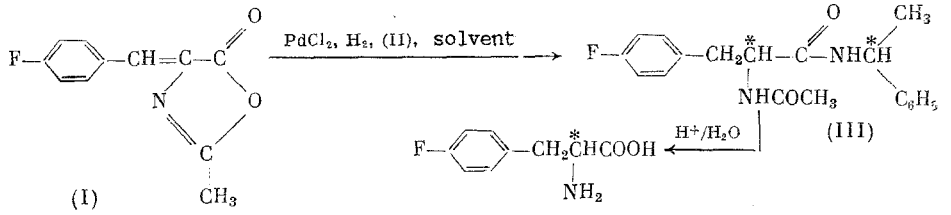
p-Fluorophenylalanine and its derivatives have antiviral [1] and antitumor activity [2]. Optically active p-fluorophenylalanine was obtained previously by cleavage of the racemate [3]. We carried out catalytic asymmetric synthesis of optically pure S-p-fluorophenylalanine by reductive aminolysis of p-fluoro-α-acetaminocinnamic acid azalactone (I).

DISCUSSION OF THE OBTAINED RESULTS

The reductive aminolysis (RA) of α-acetaminocinnamic acid azalactone in aprotic solvents in the presence of a chiral Pd catalyst gives N-acetyl-S-phenylalanine S-(−)-α-phenylethylamide, the hydrolysis of which affords S-phenylalanine [4]. When the reaction is carried out in alcohols, esters or amides are formed, in relation to the nature of the alcohol [5]. In the present paper, RA was used to synthesize optically active p-fluorophenylalanine. The RA of (I) was carried out in dimethoxyethane (DME) or isopropyl alcohol in the presence of $PdCl_2$ and H_2 with additions of S-(−)-α-phenylethylamine (II) and triethylamine (TEA).



The identification of the products and the determination of their ratio were carried out by IR and proton NMR spectroscopy. The proton signals were assigned by analogy with

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Institute of Organic Chemistry, Academy of Sciences of the USSR, Kiev. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1359-1361, June, 1987. Original article submitted October 23, 1985.

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