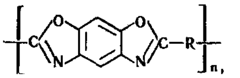
NEW MONOMERS FOR THE SYNTHESIS OF HEAT-STABLE POLYHETEROCYCLES

V. P. Evstaf'ev, G. I. Braz,
and A. Ya. Yakubovich

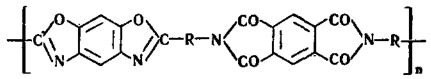
UDC 547.787.3:542.952

To obtain benzodioxazole analogs of the polypyromellitimides and polymers with alternating pyromellitimide and benzodioxazole links, we have synthesized 2,6-di(p-aminophyl)benzo[1,2-d:5,4-d']dioxazole (I), 2,6-di[p-(p'-aminophenoxy)phenyl]benzo-[1,2-d:5,4-d']dioxazole (II), N,N'-di(p-chloroformylphenyl)pyromellitdiimide (III) and N,N'-di(p-chloroformylphenyl)-2,5-dimethoxycarbonyl terephthalamide (IV). Derivatives modelling the polymers mentioned above have been synthesized from the diamines mentioned, and also from 4,6-diaminoresorcinol.

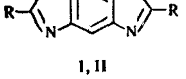
In view of the investigations that we are carrying out on the relationship between the properties of rigid-chain polymers and their structure, we have made attempts to obtain the benzodioxazole analogs of polypyromellitimides of the type



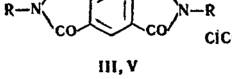
and also polymers in which pyromellitimide rings alternate with benzodioxazole rings, which have similar structures to pyromellitimide rings:



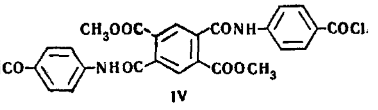
The present paper reports the synthesis of new starting materials for the creation of such polymers: 2,6-di(p-aminophenyl)benzo[1,2-d:5,4-d']dioxazole (I), 2,6-di[p-(p'-aminophenoxy)phenyl]benzo[1,2-d:5,4-d']-dioxazole (II), and N,N'-di(p-chloroformylphenyl)pyromellitdiimide (III). The poor solubility of the dichloride III in amide solvents in the cold and the difficulty that this may cause in polycondensation induced us also to synthesize N,N'-di(p-chloroformylphenyl)-2,5-dimethoxycarbonylterephthalamide (IV).



I, II



III, V



IV

I R=p-$C_6H_4NH_2$; II R=p,p'-$C_6H_4OC_6H_4NH_2$; III R=p-C_6H_4COCl; V R=p-C_6H_4COOH

The 4,6-diaminoresorcinol required for the synthesis mentioned above was first obtained in the form of the dihydrochloride [1]. However, detailed instructions for synthesis exist only for the intermediate 4,6-dinitroresorcinol [2]. We reduced the latter a) with hydrazine hydrate in the presence of Raney nickel and b) with tin in hydrochloric acid, and isolated the dihydrochloride of 4,6-diaminoresorcinol with yields of, respectively, 50-60 and 90%.

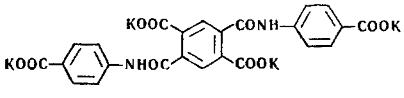
Karpov Physicochemical Institute, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 6, pp. 739-743, June, 1970. Original article submitted November 12, 1968.

The free base was isolated from the dihydrochloride by the action of sodium bicarbonate solution. When diaminoresorcinol dihydrochloride was treated with a solution of sodium acetate, instead of the expected free base its diacetate was obtained.

The diamines I and II were obtained by condensing 4,6-diaminoresorcinol dihydrochloride in polyphosphoric acid with p-aminobenzoic acid and with p-(p'-aminophenoxy)benzoic acid, respectively.

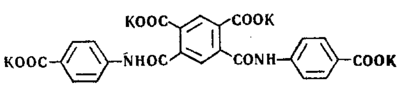
To synthesize the latter compound, the dipotassium salt of p-hydroxybenzoic acid was fused with an excess of p-chloronitrobenzene in the presence of metallic copper powder. The p-(p'-nitrophenoxy)benzoic acid obtained in this way was reduced to p-(p'-aminophenoxy)benzoic acid with hydrogen sulfide in aqueous ammonia or with hydrogen in the presence of Raney nickel.

After various unsuccesful attempts to obtain the dichloride III directly from N,N'-di(p-carboxyphenyl)-pyromellitdiimide (V), we synthesized compound III by the action of thionyl chloride on the tetrapotassium salt of N,N'-di(p-carboxyphenyl)-pyromellitdiamide (VIa or VIb).



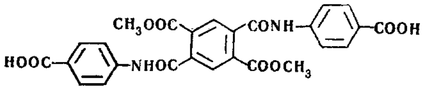
VIa

or



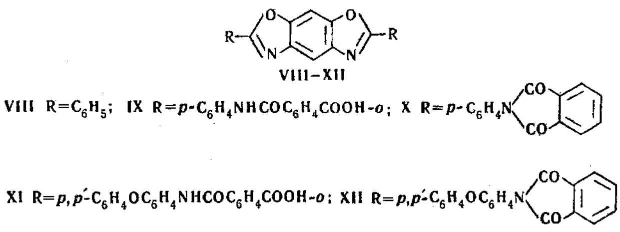
VI 6

For the synthesis of the dichloride IV, N,N'-di(p-carboxyphenyl)-2,5-dimethoxycarbonylterephthalamide (VII) was obtained by condensing 2,5-dimethoxycarbonylterephthalyl chloride [3] with p-aminobenzoic acid in dimethylacetamide. This was then converted into IV by treatment with thionyl chloride.



VII

From 4,6-diaminoresorcinol and the diamines I and II were obtained derivatives modelling the polymers intended for synthesis. Thus, 4,6-di(benzoylamino)resorcinol and 2,6-diphenylbenzo[1,2-d:5,4-d']-dioxazole (VIII) were synthesized from 4,6-diaminoresorcinol. The reaction of the diamine I with phthalic anhydride gave its N,N'-diphthalyl derivative (IX) and 2,6-di(p-phthalimidophenyl)benzo[1,2-d:5,4-d']-dioxazole (X), depending on the conditions, and likewise, the diamine II gave its N,N'-diphthalyl derivative (XI) and 2,6-di[p-(p'-phthalimidophenoxy)phenyl]benzo]1,2-d:5,4-d']dioxazole (XII).



VIII-XII

VIII $R=C_6H_5$; IX $R=p\text{-}C_6H_4NHCOC_6H_4COOH\text{-}o$; X $R=p\text{-}C_6H_4N(CO)_2C_6H_4$

XI $R=p,p'\text{-}C_6H_4OC_6H_4NHCOC_6H_4COOH\text{-}o$; XII $R=p,p'\text{-}C_6H_4OC_6H_4N(CO)_2C_6H_4$

The structures of the compounds obtained were confirmed by their IR spectra and by their interconversions.

The IR spectra of compounds III, V, X, XII, and XV each have a band in the 1780-1795 cm^{-1} region and a strong band in the 715-725 cm^{-1} region, which are characteristic for imido compounds [4] and are absent from the spectra of compounds IV, VII, IX, XI, and XVI. The spectra of the latter have bands in the 3300-3350 cm^{-1} region ($\rangle$NH) and 1660-1695 cm^{-1} (amide-I).

EXPERIMENTAL

The elementary analyses of the compounds described here were performed under the direction of K. A. Samurskii.

4,6-Diaminoresorcinol Dihydrochloride. a) To a solution of 2 g (0.01 mole) of 4,6-dinitroresorcinol [2] in 40 ml of dioxane and 10 ml of ethanol was added 2.3 mg of Raney nickel [5], and, with vigrous stirring, 10 ml (0.2 mole) of hydrazine hydrate in 10 ml of dioxane and 6 ml of ethanol was added rapidly without the temperature being allowed to rise above 40°C, after which the mixture was kept until it had become decolorized (~20 min).* Then it was slowly heated to 70°C, 0.3-ml portions of Raney nickel were added several times, in each case after the evolution gas had ceased, the hot solution was filtered from the catalyst, and the residue was washed with hot dioxane. The filtrate was treated with 3 ml of conc. HCl, a large part of the solvent was distilled off in vacuum, another 30 ml of conc. HCl was added, and the diaminoresorcinol dihydrochloride that deposited was filtered off and was twice reprecipitated from a carbon-decolorized solution in 5-7% HCl by saturating it with hydrogen chloride. The diaminoresorcinol dihydrochloride was washed with ethanol and dried. Yield 50-60%. Found, %: C 33.79; H 4.86; Cl 33.51. $C_6H_{10}Cl_2N_2O_2$. Calculated, %: C 33.83; H 4.73; Cl 33.30; N 13.15. The dry salt is stable on prolonged storage.

b) A mixture of 10 g (0.05 mole) of dinitroresorcinol, 320 ml of 18% hydrochloric acid, and 60 g of granulated tin was heated in the boiling water bath with stirring for 2 h. The whole of the dinitroresorcinol passed into the solution, and this was decanted from the residual tin and was saturated with hydrogen chloride at 0-5°C. Contrary to what is stated in the literature [1], the crystals that had deposited did not contain tin. The diaminoresorcinol hydrochloride was twice reprecipitated as described in paragraph (a). Yield 90%. Found, %: C 33.80; H 4.76; Cl 33.28; N 12.89.

4,6-Di(acetylamino)resorcinol. A saturated aqueous solution of sodium acetate free from oxygen was added to a solution of 2 g of diaminoresorcinol dihydrochloride in 30 ml of water in a current of inert gas to bring the pH to 5. The precipitate was washed with water until the reaction for chloride ion was negative and then with ethanol, and was dried in vacuum without heating. The yield of the diacetyl derivative was 2.17 g (89%), mp 183°C (decomp.).† Found, %: C 46.74; H 6.54. $C_{10}H_{16}N_2O_6$. Calculated, %: C 46.14; H 6.20.

4,6-Diaminoresorcinol. With stirring and ice–salt cooling in a current of argon, 50 ml of a 6% solution of sodium bicarbonate was added dropwise to an argon-purged solution of 4.26 g (0.02 mole) of diaminoresorcinol hydrochloride in 60 ml of water. The precipitate that deposited was filtered off, washed free from chloride ion with water which had been boiled and cooled in an atmosphere of argon and then with absolute ethanol and with ether, and was dried in vacuum at ~20°C. Yield 40-60%. 4,6-Diaminoresorcinol decomposes on heating and has no definite melting point. Found, %: C 51.58; H 5.72. $C_6H_8N_2O_2$. Calculated, %: C 51.44; H 5.75. It dissolves in cold hexamethylphosphoramide and, less readily, in other amide solvents and in water and is sparing soluble in ethyl acetate, ether, and ethanol.

The N,N'-dibenzoyl derivative was obtained by the action of benzoyl, chloride on a solution of 4,6-diaminoresorcinol in dimethylacetamide. Yield 56%, mp 314.5-315.5°C (from dimethylformamide; corrected, capillary immersed at 302°C, rate of rise of temperature 2 deg C/min). Found, %: C 68.83; H 4.72; N 8.36. $C_{20}H_{16}N_2O_4$. Calculated, %: C 68.95; H 4.63; N 8.04.

2,6-Diphenylbenzo[1,2-d:5,4-d']dioxazole (VIII). With the continuous passage of argon, 2.13 g (0.01 mole) of diaminoresorcinol hydrochloride was slowly added to 45 g of polyphosphoric acid at 120°C, and then 2.44 g (0.02 mole) of benzoic acid was added, and the mixture was heated at 250°C for 4 h, cooled to 100°C, and poured into a mixture of water and ice. The precipitate was filtered off, washed with 3% caustic potash and then with water to neutrality, and crystallized from dimethylformamide. Yield 1.6 g (50%), mp 335-336°C (corr.,sublimed). Found, %: C 76.90; H 3.88; N 9.34. $C_{20}H_{12}N_2O_2$. Calculated, %: C 76.91; H 3.87; N 8.97. The same compound was obtained by heating 4,6-di(benzoylamino)resorcinol with phosphorus oxychloride.

p-(p'-Nitrophenoxy)benzoic acid (XIII). With heating 207 g (1.5 mole) of p-hydroxybenzoic acid was dissolved in 500 ml of absolute ethanol, and to the resulting solution was added a solution of 205 g (3.1 mole) of 85% caustic potash in 600 ml of absolute ethanol. After cooling, the precipitate of the dipotassium salt of p-hydroxybenzoic acid that deposited was filtered off, washed with ethanol, and dried. With stirring, 3.5 g of metallic copper powder and 214 g (1 mole) of the dipotassium salt were added to a melt of 400 g (2.5 mole) of p-chloronitrobenzene, and the mixture was stirred at 235°C for 7 h. After cooling, the un-

---

*In the method described, the preparation of diaminoresorcinol must be carried out in a current of inert gas.

†The melting point of this substance was determined by placing capillaries in a copper block heated at various temperatures differing from one another by approximately 2°C. The minimum temperature at which the substance fused about 15-20 sec after the introduction of the capillary was taken as the melting point. The melting points of compounds I, IV, IX, and XI were determined similarly.

changed p-chloronitrobenzene was extracted with acetone, and the acetone-insoluble potassium salt of compound XIII was crystallized from 5 liters of hot water, and was then redissolved in 16 liters of cold water and the XIII was precipitated with conc. HCl. Yield 207 g (80%), mp 236-238°C. According to the literature [6], mp 236-237°C.

p-(p'-Aminophenoxy)benzoic Acid (XIV). a) Hydrogen sulfide was passed for 3 h through a suspension of 10.04 g (0.04 mole) of compound XIII in 1 liter of ammonia (d_4^{20} 0.88) at ~20°C, and the mixture was boiled until the evolution of gases ceased and the colloidal sulfur was filtered off with carbon. The filtrate was acidified first with hydrochloric acid, towards the end, with acetic acid to pH 4.5, and, for purification, the compound XIV that separated out was dissolved in 180 ml of boiling 1% HCl, the solution was filtered and left to crystallize, and the hydrochloride that deposited was again dissolved in 3% of caustic potash. The XIV was isolated from the alkaline solution as described above. Yield 2.9 g (32%), mp 194-195°C. According to the literature [6], mp 193-194°C.

b) 40.5 g (0.015 mole) of compound XIII in 400 ml of ethanol was reduced with hydrogen at ~70°C and an initial pressure of 100 gauge atm in the presence of ~6 g (two teaspoons) of Raney nickel catalyst. After the end of the reaction, the catalyst was filtered off and washed with boiling ethanol, the filtrate was evaporated to a volume of 150 ml and cooled, and the compound XIV that deposited was purified as described in paragraph (a). Yield 46%, mp 194.5-195.5°C. Additional recrystallization from ethanol raised the mp to 196°C.

2,6-Di(p-aminophenyl)benzo[1,2-d:5,4-d']dioxazole (I). With stirring, 5.32 g (0.025 mole) of diaminoresorcinol dihydrochloride was gradually added at 100-105°C to 120 g of polyphosphoric acid which had previously been heated at 200°C in a current of argon, and heating was continued until the evolution of hydrogen chloride ceased (~2 h). Then 6.85 g (0.05 mole) of p-aminobenzoic acid was added at 110-120°C, and the mixture was stirred at 120°C for 4 h, after which the temperature was raised to 150°C over 2 h and, with continuous stirring, it was heated at 150°C for 10 h and at 170°C for another 1.5 h. Then it was cooled to 100°C and poured into water containing ice, and the mixture was brought to a volume of 6 liters allowed to stand in tall cylinders, the upper aqueous layer containing no solid phase was separated off, and the precipitate was filtered off with suction, transferred into 200 ml of 5% ammonium carbonate solution, filtered off again with suction after stirring, mixed with 200 ml of methanol, filtered, and washed twice with methanol. After this treatment, the precipitate was readily separated on the filter both from water and from methanol. It was washed with water until the reaction for ammonium ion (Nessler's reagent) was negative and then with methanol again, and was dried. The yield of I was 7.8 g (92%). For purification, the I was dissolved in 160 ml of dimethyl sulfoxide heated to 80°C, and then 560 ml of cold toluene was added, the mixture was cooled to 0°C, and the brown precipitate that deposited was filtered off with suction. The filtrate was treated in the cold with another 900 ml of toluene, and the mixture was left at 0-5°C for a day, and was then filtered and the residue of diamine was washed with methanol. This gave 4 g of yellow crystalline I, mp 418°C (corr., decomp.). The substance is soluble in hexamethylphosphoramide and dimethylacetamide and is insoluble in acetone and hydrochloric acid. Found, %: C 70.07; H 4.24; H 16.13. $C_{20}H_{14}N_4O_2$. Calculated, %: C 70.17; H 4.12; N 16.36.

The melting point and solubility properties of compound I differ from those of the substance previously [7] ascribed the structure I, apparently erroneously.

2,6-Di[p-(p'-aminophenoxy)phenyl]benzo[1,2-d:5,4-d']dioxazole (II) was obtained under precisely the same conditions as the diamine I, but was purified by crystallization from pyridine (1:70). Yield 65%. Beige microscopic needles, mp 290-292°C (decomp.). Found, %: C 73.00; H 4.28; N 10.62. $C_{32}H_{22}N_4O_4$. Calculated, %: C 73.00; H 4.21; N 10.64. The substance is soluble on heating in dimethylacetamide, dimethyl sulfoxide, and benzonitrile, and is insoluble in triethylamine.

N,N'-Di(p-carboxyphenyl)pyromellitdiimide (V) was obtained as described by Gitis et al. [8]. The substance does not melt below 500°C (corr.), dissolves in aqueous caustic potash in the cold with the opening of the ring, is moderately soluble in sulfuric acid, and dissolves with difficulty in boiling dimethyl sulfoxide, boiling tetramethylene sulfone, and boiling N-methylpyrrolidone.

N,N'-Di(p-ethoxycarbonylphenyl)pyromellitdiimide (XV) was obtained by condensing ethyl p-aminobenzoate with pyromellitic dianhydride in boiling dimethylformamide. Yield 60%; elongated light yellow plates (from tetramethylene sulfone), not melting below 400°C. Found, %: C 65.87; H 3.99; N 5.20. $C_{28}H_{20}N_2O_8$. Calculated, %: C 65.61; H 3.93; N 5.47. The substance is sparingly soluble in dimethyl sulfoxide and dimethylacetamide.

N,N'-Di(p-carboxyphenyl)pyromellitdiamide (XVI). At 20°C, 10.96 g (0.08 mole) of p-aminobenzoic acid was added to a solution of 8.72 g (0.04 mole) of pyromellitic dianhydride in 120 ml of anhydrous dimethylformamide. On the following day, 80 ml of dimethylformamide was distilled in vacuum, 180 ml of benzene was added to the suspension formed, and the precipitate was filtered off. The yield of XVI was 16.2 g (82%); it did not melt below 400°C. Found, %: C 58.37; H 3.48; N 5.41. $C_{24}H_{16}N_2O_{10}$. Calculated, %: C 58.55; H 3.28; N 5.69. The action of thionyl chloride on XVI in dimethylformamide solution formed compound V.

Tetrapotassium Salt of Compound XVI (VI). At ~20°C, 7.4 g (0.15 mole) of XVI was dissolved in 57 ml (0.15 mole) of 2.64 N KOH, and 170 ml of ethanol was added, after which the precipitate of XVI that had deposited was filtered off, washed with ethanol, and dried at 130°C (3 mm). Yield 6 g (60%). Found, %: C 43.54; H 2.70; K 23.72; N 3.73. $C_{24}H_{12}K_4N_2O_{10} \cdot H_2O$. Calculated, %: C 43.50; H 2.13; K 23.59; N 4.23.

N,N'-Di(p-chloroformylphenyl)pyromellitdiimide (III). A mixture of 5.8 g (9 mmoles) of compound VI was boiled with 50 ml of thionyl chloride for 2 h, and the excess of the latter was distilled off. Colorless microscopic needles (from bromobenzene) not melting below 400°C. Yield 37%. Found, %: C 57.80; H 2.39; Cl 13.97; N 6.04. $C_{24}H_{10}Cl_2N_2O_6$. Calculated, %: C 58.45; H 2.04; Cl 14.37; N 5.68.

N,N'-Di(p-carboxyphenyl)-2,5-dimethoxycarbonylterepthalamide (VII). With stirring, 9.6 g (0.03 mole) of 2,5-dimethoxycarbonylterephthalyl chloride [3], mp 134-137°C (from benzene–hexane) was gradually added to a solution of 8.2 g (0.06 mole) of p-aminobenzoic acid in 150 ml of dimethylacetamide. The temperature rose spontaneously to ~30°C. Stirring was continued at ~20°C for another 2 h, and 200 ml of water was added. The precipitate was filtered off, washed with water until the reaction for chloride ion was negative, and then with ethanol, and was dried. For purification, the substance was reprecipitated from 100 ml of dimethylacetamide with 700 ml of benzene. Yield 9.4 g (60%); it did not melt completely below 450°C (corr.). Found, %: C 60.20; H 3.81; N 5.85. $C_{26}H_{20}N_2O_{10}$. Calculated, %: C 60.01; H 3.88; N 5.38.

N,N'-Di(p-chloroformylphenyl)-2,5-dimethoxycarbonylterephthalamide (IV). A mixture of 5.2 g (0.01 mole) of compound VII, 52 ml of thionyl chloride, and 0.3 ml of dimethylformamide [9] was boiled for 5 h. The precipitate was filtered off from the hot solution, treated twice with fresh boiling thionyl chloride, and washed with benzene and ether. Yield 60%, colorless needles. It melted at 298°C (corr.) with the evolution of gas and then resolidified. Found, %: C 54.74; H 3.92; Cl 12.94; N 4.97. $C_{26}H_{18}Cl_2N_2O_8$. Calculated, %: C 56.03; H 3.25; Cl 12.72; N 5.03. When an attempt was made to recrystallize IV from anhydrous dioxane, nitrobenzene, or cyclohexanone, the substance underwent change.

2,6-Di(p-phthalylaminophenyl)benzo[1,2-d:5,4-d']dioxazole (IX). At ~20°C, 0.59 g (4 mmoles) of phthalic anhydride was added to a solution of 0.68 g (2 mmoles) of diamine I in 20 ml of dimethylacetamide. On the following day, compound IX was precipitated with water and washed with methanol. Yield 92%. For purification, the substance was reprecipitated from dimethylacetamide with toluene. Compound IX does not melt completely below 430°C (corr.). Found, %: C 66.88; H 3.56; N 8.53. $C_{36}H_{22}N_4O_8$. Calculated, %: C 67.72; H 3.47; N 8.77.

2,6-Di(p-phthalimidophenyl)benzo[1,2-d:5,4-d']dioxazole (X). A mixture of 0.68 g (2 mmoles) of the diamine I and 0.65 g (4.4 mmoles) of phthalic anhydride in 45 ml of nitrobenzene was boiled for 20 h and cooled, and the product was filtered off. Yield 85%, mp 461°C (corr., from N-methylpyrrolidone). Found, %: C 71.82; H 3.15; N 8.95. $C_{36}H_{18}N_4O_6$. Calculated, %: C 71.76; H 3.01; N 9.30. The substance is sparingly soluble in boiling tetramethylene sulfone, N-methylpyrrolidone, nitrobenzene, and hexamethylphosphoramide.

2,6-Di[p-(p'-phthalylaminophenoxy)phenyl]benzo[1,2-d:5,4-d']dioxazole (XI). 0.52 g (1 mmole) of the diamine II was dissolved in 16 ml of dimethylacetamide at 110°C, and the solution was cooled to ~30°C, after which 0.296 g (2 mmoles) of phthalic anhydride was added, the mixture was left overnight, and the XI was precipitated by the addition of 32 ml of toluene. Yield 86%, mp 368°C [corr., determined for 4,6-di(acetylamino)resorcinol; on slow heating, it was converted into XII and melted at 378°C]. Found, %: C 70.38; H 3.63; N 6.50. $C_{48}H_{30}N_4O_{10}$. Calculated, %: C 70.06; H 3.67; N 6.81. Compound XI is readily soluble in pyridine, dimethyl sulfoxide, and dimethylacetamide.

2,6-Di[p-(p'-phthalimidophenoxy)phenyl]benzo[1,2-d:5,4-d']dioxazole (XII). A solution of XII in dimethylacetamide obtained as described above, from 1 mmole of II and 2 mmoles of phthalic anhydride was boiled for 3 h. About 15 min from the beginning of boiling, coarse crystals of XII deposited. Yield 87%, mp 377-378°C (corr., from nitrobenzene). Found, %: C 71.80; H 3.44; N 6.82. $C_{48}H_{27}N_4O_8$. Calculated, %:

C 73.28; H 3.33; N 7.12. The compound is soluble in boiling sulfolane, nitrobenzene, and N-methylpyrrolidone, inclusively.

LITERATURE CITED

1. P. G. W. Typke, Ber., 16, 551, 1883.
2. W. Borsche and E. Feske, Ber., 61, 690, 1928.
3. V. Bell and R. Jewell, J. Polymer Sci., A-1, 5, 3043, 1967.
4. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, J. Polym. Sci., A3, 1373, 1965.
5. J. Houben, Die Methoden der organischen Chemie [Russian translation], Moscow, Vol. 4, Book 2, p. 1054, 1949.
6. C. Häusserman and E. Bauer, Ber., 29, 2083, 1896.
7. O. Kym, Ber., 44, 2919, 1911.
8. S. S. Gitis, V. M. Ivanova, S. A. Nemleva, and Z. N. Seina, ZhOrKh, 2, 1265, 1966.
9. H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, Helv. Chim. Acta, 42, 1653, 1959.