Journal of Fluorine Chemistry, 53 (1991) 327–338

Received: January 16, 1991; accepted: July 8, 1991

AROMATIC DIAMINES OF HIGH FLUORINE CONTENT

S. NADJI, G.C. TESORO* and S. PENDHARKAR

Polytechnic University, Brooklyn, NY 11201 (U.S.A.)

ABSTRACT

Fluorine-containing aromatic diamines have been synthesized as monomers for an investigation of polyimides of low dielectric constant. For most compounds, the synthetic route has been based on nucleophilic aromatic substitution of alcohols and phenols, on appropriate aromatic nitro compounds, and subsequent hydrogenation of the dinitro compounds obtained. The separation and purification of products was attained by flash column chromatography, and characterization of the products by molecular weight determination and elemental analysis.

INTRODUCTION

Aromatic polyimides are an important class of thermally stable polymers used as insulating layers between levels of thin film wiring in high density electronic packaging applications. The increasing demands of this application have stimulated extensive research on polyimide structures that can exhibit the

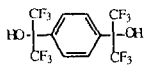
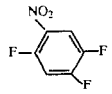
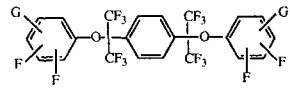
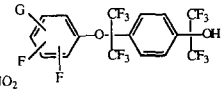
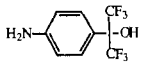
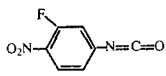
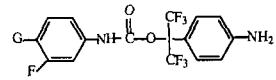
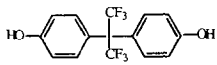
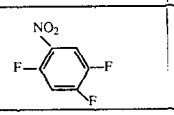
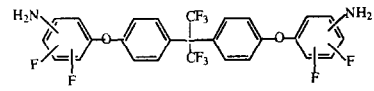
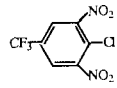
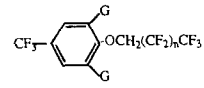
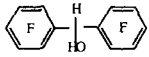
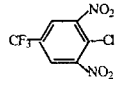
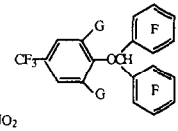
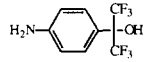
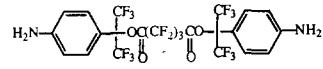
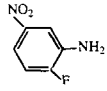
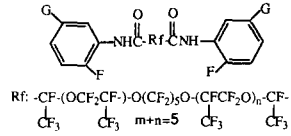
* To whom correspondence should be addressed.

0022-1139/91/$3.50

required balance of thermooxidative stability,mechanical properties over the range of temperatures used in device manufacturing, and electrical properties [1,2]. Research on polyimides of low dielectric constant that simultaneously meet other essential requirements has been significant in recent years, and the incorporation of fluorinated segments in the polyimide macromolecules has been investigated. Known fluorine-containing diamines explored for polyimide synthesis have been those containing perfluoroalkylene groups [3], some aromatic diamines containing a hexafluoroisopropylidene function [4], perfluoro aromatic diamines [5] and aromatic diamines in which fluorinated rings were linked to aminophenyl groups by oxygen or methylene [6]. The objective of the work reported here has been to synthesize new fluorine-containing aromatic diamine structures for the study of polyimides where low dielectric constant would be attained without sacrifice in other essential properties. The rationale for the specific compounds synthesized has been based in part on availability of starting materials, and also on other considerations including aromatic structure for thermal stability, basicity of the amine function and fluorine content in the diamines for maximum effect on electrical properties. Structures of reactants and products are summarized in Scheme I. The overall strategy has been based on nucleophilic aromatic substitution of alcohols and phenols (1-6), on fluorinated aromatic nitro compounds (9-11), and on subsequent hydrogenation of the resulting dinitro compounds. However, other types of reactions have also been explored. For example, diamine (26) was obtained by esterification of perfluoroglutaric acid (7) and diamine (28) was prepared by reaction of the perfluorodiacid fluoride (8) with 2-fluoro-5-nitroaniline (12). Details of the synthesis are given in the Experimental Section below. However, several points warrant comment.

RESULTS AND DISCUSSION

Nucleophilic aromatic substitution of bis alcohol (1) on trifluoronitrobenzene (9) gave a mixture of di(13) and mono-substituted products (14). These were separated and purified

#	Alcohol/Phenol/Acid/Acid fluoride	#	Nitro/Amino compounds	#	Products
1		9		13 15 14 16	 G= NO_2 G= NH_2  G= NO_2 G= NH_2
2		10		17 18	 G= NO_2 G= NH_2
3		9		19	
4 5	$CF_3(CF_2)_2CH_2OH$ $CF_3(CF_2)_6CH_2OH$	11		20 21 22 23	 n=2 G= NO_2 n=2 G= NH_2 n=6 G= NO_2 n=6 G= NH_2
6		11		24 25	 G= NO_2 G= NH_2
7		2		26	
8		12		27 28	 Rf: -CF-(OCF_2CF-)-$O(CF_2)_5O$-($CFCF_2O$)$_n$-CF- m+n=5 G= NO_2 G= NH_2

Scheme 1.

efficiently on a mg. scale. However, separation was troublesome when attempted on a gram scale. Subjecting the crude mixture to hydrogenation gave a mixture of the desired diamine (15) and an amino alcohol (16) which could be separated by flash-column chromatography. The compounds (15) and (16) showed similar mass fragmentation patterns and characterization was possible only by molecular weight determination and elemental analysis. Similar observations were experienced in the reaction of the bis-phenol (3) with the trifluoronitrobenzene (9). Careful analysis of mass, NMR and IR spectra for both products - diamines (15) and (19) - did not establish whether substitution had occurred on the para or the ortho fluorine in the nitrobenzene ring and the diamine products may thus be mixtures of isomers.

Addition of hexafluoroacetone trihydrate to freshly distilled aniline at 0°C and subsequent refluxing for 2 hours according to the published procedure [7] afforded the amino alcohol (2) in 25% yield. The availability of this amino alcohol and the perception of the ease of nucleophilic addition of alkoxides and phenoxides to the isocyanate functionality prompted us to try the addition of the sodium salt of the amino alcohol (2) with 3-fluoro-4-nitrophenyl isocyanate (10) at 0°C. The desired nitro amino compound (17) was obtained in 41% yield and the corresponding diamine (18) was isolated in quantitative yield upon hydrogenation.

In connection with another synthetic project in progress in our laboratory, we realized the interesting activity of compound (11) toward nucleophilic aromatic substitution. Our experience with this compound showed that the chlorine atom at position 4 can easily be displaced with carbanions even at 0°C. Thus it was expected that fluoroalcohols (4), (5) and (6) would likewise displace the chlorine atom at low temperatures. When dinitro compound (11) was injected into a suspension of the sodium salt of alcohol (4), a deep red solution was immediately obtained. Stirring of the mixture for 2 hrs. at room temperature showed no trace of the starting dinitro compound as judged by TLC, and the desired product (20) was separated by flash chromatograph in 59% yield. Similarly, alcohol (5) gave the desired product (22) in 45% yield (a small amount of the starting material was also isolated). Hydrogenation of (20) and (22) with catalytic amount of 10% Pd-C afforded diamino derivatives (21) and (23) in 88 and 93% yield respectively.

Reaction of the perfluorobenzhydrol (6) with compound (11) also proceeded smoothly and the dinitro compound (24) was obtained in 62% yield. However, reduction yielded several unidentified products in addition to the desired diamine (25).

The diacid fluoride (8) recently became available from a commercial source*. Presence of two active acid fluoride groups made it possible to attach two nitroaromatic groups to it by either an amide or an ester linkage. Thus, treating the diacid fluoride (8) with 2-fluoro-5-nitroaniline (12) under coupling conditions afforded the dinitro compound (27) in 36% yield. The diamino compound (28) was obtained (89%) by hydrogenation of (27) with 10% Pd-C. Characterization of the products was based on their mass spectra. Although because of the polymeric nature of the starting diacid fluoride (8) molecular ion peak cannot be assigned accurately, the comparison of the mass spectra of compounds (27) and (28) can help the characterization of products. Dinitro derivative (27) is expected to have a molecular weight of 1316 based on the manufacturer specification for the diacid fluoride (8). However, the mass spectrum of the dinitro derivative (27) shows not only a peak for 1316, but two other peaks of 1329 and 1346, the latter one being the parent peak. Based on this data, the mono nitro-monoamino derivative should have three peaks at 1316 (parent peak), 1299 and 1286 and the diamino derivative 28 at 1286 (parent), 1269 and 1256. All the major peaks observed in the mass spectra of compounds (27) and (28) are in agreement with our expectations.

Another approach to include an aliphatic chain of fluorinated hydrocarbon to an aromatic amino compound is the reaction of amino alcohol (2) with perfluoroglutaric acid (7). While there are potential problems in using the amino alcohol (2) for nucleophilic substitution reaction from the hydroxyl end without interference from the amino end group, we found that esterification of (2) with perfluoroglutaric acid is smooth, and gives the desired diamino compound (26) as a single product. Mass spectrum fragmentation of the product convincingly points to the expected structure.

---

* PCR Inc., Gainesville, FL.

EXPERIMENTAL

Unless otherwise noted, starting materials were obtained from commercial suppliers and were used without further purification. TLC was run on Aldrich precoated Silica gel 70FM plates. Merck Silica gel 60 (200-400 mesh) was used for column chromatography, N,N-Dimethylformamide (DMF) was dried by distillation from calcium hydride and kept over 4 Å molecular sieves. Triethylamine was dried by distillation from calcium hydride. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone. Methylene chloride was freshly distilled from calcium hydride. ^{1}H NMR spectra (in CD_3COCD_3)are referenced to internal TMS (JEOL, 90 MHz). High resolution mass spectra were obtained with a Kratos MS 25 instrument

p-Di[2,2(4^{1}aminodifluorophenoxy)1,1,1,3,3,3,hexafluoropropyl] benzene (15)

To a suspended mixture of sodium hydride (60%, 50 mg, 1.25 mmol) in THF (2 ml) at 0°C was added a,a,a^1,a^1 tetra (trifluoromethyl)-1,4-benzene dimethanol (1) (225 mg, 0.5 mmol). The mixture was stirred for 30 min. at 0°C and then 2 hrs. at room temperature. The solvent was removed under pressure and the residue was suspended in dry DMF. 1,2,4-trifluoro-5-nitrobenzene (9) (130 µ l, 1 mmol) was then injected. The mixture was stirred for 30 min. at room temperature and refluxed for another 30 min. The solvent was removed by distillation under reduced pressure and the residue was partitioned between ethyl acetate and saturated aqueous NaCl. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue on silica gel (9:1 hexane/EtOAc) gave 205 mg(56.6%) of the desired dinitro product 13 (Rf 0.31). MS m/e(relative intensity) 724 (M+, 4%) 550 (35%) 393 (100%) 307 (27%) 254 (25%).NMR δ 7.5) IR (KBr) 1712.6, 1616.3, 1539.2, 1080.1 cm^{-1}. % Calcd. for $C_{24}H_8N_2O_6F_{16}$: C, 39.79; H, 1.11. Found C, 40.01; H, 1.13.

Hydrogenation. The dinitro product was dissolved in EtOH and a catalytic amount of 5% Pd-C was added. The mixture was stirred

under an atmosphere of hydrogen gas at room temperature for 18 h. The catalyst was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was flash chromatographed (**EtOAc-hexane 1:4**) to give a pale yellow liquid. The yellow liquid residue solidified on standing (182 mg, 96.8%) Rf **0.21. MS**, m/e (relative intensity) 70% (M+K, 7%) 665 (M+1, 13%) 361 (8%) 144 (100%) 138 (31%); IR (KBr) 3471, 3379.3, 3225 NH), 1708, 1523.8, 1508.3, 1438.9, 1238.3, 1172.7 (cm^{-1}) % Calcd for $C_{24}H_{12}N_2O_2F_{16}$: C, 44.05; H, 0.308. Found: C, 44.15, H, 0.299.

N-(m-Amino-p-fluorophenyl)2.2(p-aminophenyl)hexafluoropropyl carbamate (18)

To a suspended mixture of NaH (60%, 98 mg, 2.4 mmol) in THF (3 ml) at 0°C was added the aminoalcohol (2) (526 mg, 2 mmol). The mixture was stirred at 0°C for 15 min. **3-Fluoro-4-nitrophenyl isocyanate** (10) (250 µl, 2 mmol) was then injected. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate and sat. aq. NH_4Cl. The organic layer was dried ($MgSO_4$), evaporated and flash chromatographed on silica gel (**EtOAc-hexanes** 2:3). The major product (361 mg, 41%) Rf 0.31 proved to be the desired nitro-amino compound (17). MS m/e (relative intensity) 441 (M+, 22%) 259 (15%), 190 (35%), 150 (100%). % Calcd. for $C_{16}H_{10}N_3O_4F_7$: C, 43.55; H, 2.28. Found: C, 43.01; H, 2.32. ^{1}HNMR δ 8.50 (M, 2H), 7.69 (S, 4H), 7.39 (2H).

Hydrogenation. The nitro-amino compound (17) (300 mg, 0.68 mmol) was dissolved in methanol and a catalytic amount of 10% Pd-C was added. The mixture was stirred under an atmosphere of hydrogen gas at room temperature for 14 h. The catalyst was removed by filtration and the solvent was evaporated to give the diamino compound (18) as a white powder (262 mg, 94%). ^{1}HNMR (100 MHz, δ 8.31 (S, 1H), 8.05 (S, 1H), 7.17-6.61 (m, 5H), 4.62 (b, 2H). MS m/e (relative intensity) 412 (M+1, 100%), 392 (38%), 333 (20%). IR (KBr) 3371, 3001, 1712, 1512, 1423, 1222, 1188 cm^{-1}. % Calcd. for $C_{16}H_{12}N_3O_2F_7$: C, 46.72; H, 2.94. Found: C, 47.01; H, 3.21.

2,2 Bis[p-4^1-amino-difluorophenoxy phenyl]-1,1,1,3,3,3-hexafluoropropane (19)

To a suspended mixture of sodium hydride (60%, 1.16 g, 29 mmol) in dry THF (25 ml) at 0°C was injected a solution of 2,2 bis [4-hydroxyphenyl] hexafluoropropane (3) (4.7 g, 14 mmol) in dry THF (15 ml). The mixture was allowed to warm up to room temperature and stirred for 30 min. The solvent was removed under reduced pressure and dry DMF (20 ml) was added to the white solid residue. The suspended mixture was stirred at room temperature for 30 min. and then cooled to 0°C. To this cold mixture a solution of the 1,2,4-trifluoro-5-nitrobenzene (9) (5 g, 28.2 mmol) in DMF (5 ml) was added slowly. Gradually the white residue dissolved and a clear yellow solution was obtained. The mixture was refluxed for 45 min. DMF was removed by distillation under reduced pressure, and the brown residue was flash chromatographed on silica gel (**EtOAc-hexanes**, 3:2). The fraction with Rf 0.29 was separated (2.18 g, 24%).

Hydrogenation. The above dinitro compound (400 mg; 0.61 mmol) was dissolved in absolute ethanol and a catalytic amount of 10% Pd/C was added. The mixture was stirred under an atmosphere of hydrogen gas overnight. The catalyst was removed by filtration and the solvent was evaporated on rotovapor. The brownish residue was flashed with **EtOAc-hexane** 3:7 to give 250 mg (68.8%); Rf 0.37 of a light yellow liquid. IR (KBr) 3471, 3379, 3225, 1709, 1528, 1508, 1238, 1207 cm^{-1}. % Calcd. for $C_{27}H_{16}N_2O_2F_{10}$: C, 54.92; H, 2.73. Found: C, 54.71; H, 2.63.

4-Trifluoromethyl-2,6 diaminophenyl 2^1, 3^1, 4^1 - heptafluorobutyl ether (21)

To a suspended mixture of sodium hydride (60%, 173 mg, 4.45 mmol) in THF (10 ml) was injected a THF (2 ml) solution of the fluoroalcohol (4) (830 mg. 415 mmol) at 0°C. The mixture was stirred for 1 h. A solution of the dinitro compound (11) (1.05 g, 4 mmol) in THF (2 ml) was then added. The mixture was stirred for 3 h at room temperature and then quenched with sat. aq.

NH_4Cl. Extraction with ethyl acetate, drying ($MgSO_4$), and evaporation of the extract gave a brown residue. Flash chromatography of the residue on silica gel (**EtOAc/hexane**, 3:1) afforded the desired product (20) (1.02 g, 59%). MS m/e (relative intensity) 434 (M+, 16%) 415 (15%) 236 (100%) 189 (25%) 159 (20%) 131 (15%). IR (KBr), 1712, 1361, 1229, 1122 cm^{-1}. % Calcd. for $C_{11}H_4N_2O_5F_{10}$: C, 35.30; H, 2.15. Found: C, 35.15; H, 2.32.

Hydrogenation. The dinitro compound (435 mg, 1 mmol) was dissolved in absolute ethanol (30 ml) and a catalytic amount of 10% Pd-C was added. The mixture was stirred under an atmosphere of hydrogen gas for 18 h. The catalyst was removed by filtration. Evaporation of the ethanol gave a yellow residue. Flash chromatography on silica gel (EtOAc/hexane 3:2) gave the diamino compound (21) (330 mg, 88%). Rf. 0.15. IR (KBr) 3491, 3379, 2962, 1739, 1716, 1373, 1226, 1168, 1126, 1049 cm^{-1}. % Calcd. for $C_{11}H_8N_2OF_{10}$: **C, 35.31; H, 2.15.** Found: C, 35.01; H, 2.50.

4-Trifluoromethyl-2,6-diaminophenyl $2^1$2", $3^1$3" - 4^1, 4" - $5^1$5" - $6^1$6", 7^1, 7", 8^1, 8" , 8^1, 8", 8^1" nonafluoro octyl ether (23)

To a suspended mixture of sodium hydride (60%, 5.2 mmol, 220 mg) in THF (10 ml) was added the fluoroalcohol (5) **(5 mmol, 2 g)** at 0°C. The mixture was stirred for 1 h and a solution of 4-chloro-3,5-dinitrobenzene trifluoride 11 (5 mmol, 1.44 g) in THF (5 ml) was added. The mixture was allowed to warm up slowly to room temperature (3 h). The mixture was quenched with sat. aq. NH_4Cl and extracted with ethyl acetate. The extract was dried ($MgSO_4$) and concentrated in vacuo. The residue was subjected to column flash chromatography (EtOAc-hexanes 1:9). The dinitro product 22 was obtained in 45% yield (1.42 g) as a yellow powder. MS m/e (relative intensity) 634 (M+, 18%) 615 (36%)236 (100%) 189 (10%) 131 (8%). IR (KBr) 1716, 1361, 1229, 1145 cm^{-1}. % Calcd. for $C_{15}H_4N_2O_5F_{18}$: C, 28.40; H, 0.63. Found: C, 28.90; H, 0.42.

Hydrogenation. The above dinitro compound (1 g, 1.57 mmol) was dissolved in absolute ethanol and a catalytic amount of 10% Pd/C

was added. The mixture was stirred under an atmosphere of hydrogen gas overnight. The catalyst was removed by filtration and the ethanol was evaporated under vacuum. The residual diamino compound was solidified under high vacuum. The desired diamine (23) was further purified by recrystallization from acetone (836 mg, 93%) **Rf(EtOAc/hexane)** 1:9), 0.51. % Calcd. for $C_{15}H_8N_2OF_{18}$: C, 31.41, H, 1.40. Found: C, 31.83; **H, 1.65.**

4-Trifluoromethyl-2,6 dinitrophenyl-di-perfluorophenyl methyl ether (0-[2,6-Dinitro-4-trifluoromethylphenyl] decafluorobenzhydrol (24)

To a solution of hexamethyl disilazene (3 mmol), 611µl L) in THF (5 ml) at -78°C was injected n-BuLi (1.8 M soln., 3 mmol, 1.875 ml). The mixture was stirred at -78°C for 5 min., at room temperature for 30 min. and then cooled down again to -78°C. Decafluorobenzhydrol (6) (3 mmol, 1.08 g) was injected and the mixture was stirred for 10 min. A solution of 4-chloro-3, 5-dinitrobenzene trifluoride (11) (3 mmol, 811 mg) in THF (2 ml) was added. The mixture was allowed to warm up to room temperature (30 min.), and then refluxed for 30 min. The mixture was extracted with dilute HCl-ethyl acetate. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the yellow residue with EtOAc-hexanes, 9:1, gave a yellow solid. Rf 0.12. The yellow solid was further purified with stirring in 25 ml of a 9:1 mixture of hexane-EtOAc. The yellow insoluble material, the desired dinitro compound was filtered off (1.1 g, 62%). MS m/e (relative intensity) 364 (10%) 347 (6%) 251 (100%) 232 (7%) 189 (16%) 159 (21%). ^{1}HNMR δ 770 (m, 2H), 6.6 (S.1 H). % Calcd. for $C_{20}H_3N_2O_5F_{13}$: C, 40.29; H, 0.50. Found: C, 40.61; H, 0.56; IR (KBr), 1712, 1635, 1550, 1323, 1180, 1126, 1014 cm^{-1}.

Bis[2-(4-aminophenyl)hexafluoro-propyl] hexafluoroglutarate (26)

Dicyclohexylcarbodiimide (400 mg, 2 mmol) was dissolved in dry methylene chloride (5 ml). Amino alcohol (2) (264 mg, 1 mmol) and perfluoroglutaric acid (7) (240 mg, 1 mmol) were then added successively. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue was partitioned

between ethylacetate and aq sat. NaCl. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue on silica gel with ethyl acetate gave the desired product as a white solid (368 mg, 51%) Rf. 0.21 MS m/e (relative intensity) 722 (M+, 6%) 465 (21%) 377 (19%) 300 (28%) 259 (20%) 224 (100%). IR (KBr) 3410, 2931, 3858, 1689, 6139, 1600, 1384, 1226, 1215, 1149, 1041 cm^{-1}. % Calcd. for $C_{23}H_{12}N_2O_4F_{18}$; C, 38.24; H, 1.67. Found: C, 38.85; H, 1.52.

Bis (fluoro-aminophenylamide)of a poly-perfluoropropylene oxide (28)

To a solution of 2 fluoro-5-nitroaniline (12) (157 mg, 1 mmol) and triethylamine (141 µ l, 1 mmol) in dry methylene chloride (5 ml) at 0°C was added slowly the diacid fluoride (8) (300 µ l, 0.5 mmol). The mixture was allowed to warm up to room temperature slowly (2.5 h) with stirring. The mixture was treated with saturated aq. $NaHCO_3$ (15 ml) and extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was flash chromatographed on silica gel (ethyl acetate-hexane 1:3) to give a pale yellow powder (27) (475 mg, 36%). Rf 0.41. MS m/e (relative intensity) 1346 (M+, 100%) 1329 (63%) 1316 (24%) 1286 (8%) 449 (52%). IR (KBr) 1708, 1361, 1246, 1222 cm^{-1}.

Hydrogenation. The above dinitro compound (475 mg, 0.35 mmol) was dissolved in absolute ethanol and a catalytic amount of 10% Pd-C was added. The mixture was stirred under an atmosphere of hydrogen gas for 24 hr. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure to give the diamino compound (28) as a white powder (400 mg, 89%). MS m/e (relative intensity) 1327 (M+K, 5%) 1299 (M+Na, 10%) 1287 (M+1, 100%) 1121 (8%) 419 (7%) 253 (15%). IR (KBr) 3435, 3445, 3311, 1708, 1534, 1419, 1303, 1246, 1033, 983 cm^{-1}.

2,2 bis [p-3^1-Fluoro-4^1nitrophenyl carbamato)phenyl]1,1,1,-3,3,3-hexafluoropropane (30)

2,2 Bis [4-hydroxyphenyl] hexafluoropropane (3) (676 mg. 2 mmol) was dissolved in THF (2.5 ml) and the mixture was stirred

at -78°C. n-BuLi (1.6M, 2.5 ml, 4 mmol) was added dropwise. The mixture was allowed to warm up to room temperature. The mixture was cooled down to -78°C and treated dropwise with 3-fluoro-4-nitrophenyl isocyanate (10) (0.500 μ 1, 4 mmol). The mixture was stirred at -78°C for 1 h and at -20°C for 30 min. The mixture was quenched with sat. aqueous NaCl (5 ml) and acidified with dilute HCl, then extracted with EtOAc. The extract was dried ($MgSO_4$) and concentrated under reduced pressure. The residual yellow solid was purified by flash chromatography on silica gel (EtOAc-hexane 2:3) to obtain the desired dinitro compound (30) as a yellow solid (574 mg, 41%) Rf 0.62.

ACKNOWLEDGEMENT

We wish to express our appreciation to the IBM Corporation (East Fishkill Facility) for financial support and for permission to publish this work. We thank Dr. Haban Sachdev of IBM for helpful discussions and suggestions in the course of this work.

REFERENCES

1 'Polyimides--Synthesis, Characterization and Applications', Vol. 1 and 2 (K.L. Mittal, Editor), Plenum Press, N.Y., 1984.

2 C. Feger, M. Khojasteh, J.E. McGrath, (Eds), 'Polyimides-Materials, Chemistry and Characterizations', Elsevier Science, Amsterdam, 1989.

3 J.P. Critchley, P.A. Grattan, M.A. White, J.S. Pippett, J. Polym. Sci A-1 10, (1972) 1789; 1809.

4 P.E. Cassidy, T.M. Aminabhavi, J.M. Farley, Reviews in Macromolecular Chem & Phys C29 (2 & 3) (1989) 394.

5 G. Hougham, G. Tesoro, J. Shaw, in reference [2] p. 465.

6 E.F. Kolchina, L.N. Ogneva, O.P. Sheremet, T.N. Gerasimova, E.P. Fokin, Izv Sib. Otd, Akad. Nauk SSSR, Ser. Khim Nauk 2 (1981), 122.

7 B.S. Farah, F.E. Gilbert, J.P. Sibilia et al, J. Org. Chem. 30 (1965) 998; 1001.