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SYNTHESIS OF REACTIVE FLUOROALIPHATIC DIAMINES

by

J. R. Griffith, A. E. Mera and K. Baum

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SYNTHESIS OF REACTIVE FLUOROALIPHATIC DIAMINES

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SUMMARY

The synthesis of reactive fluoroaliphatic diamines has been accomplished through the use of peptide blocking group and coupling techniques. Also, the synthetic route to these diamines and their dihydrobromide salts has been improved over that of a recently published procedure.

INTRODUCTION

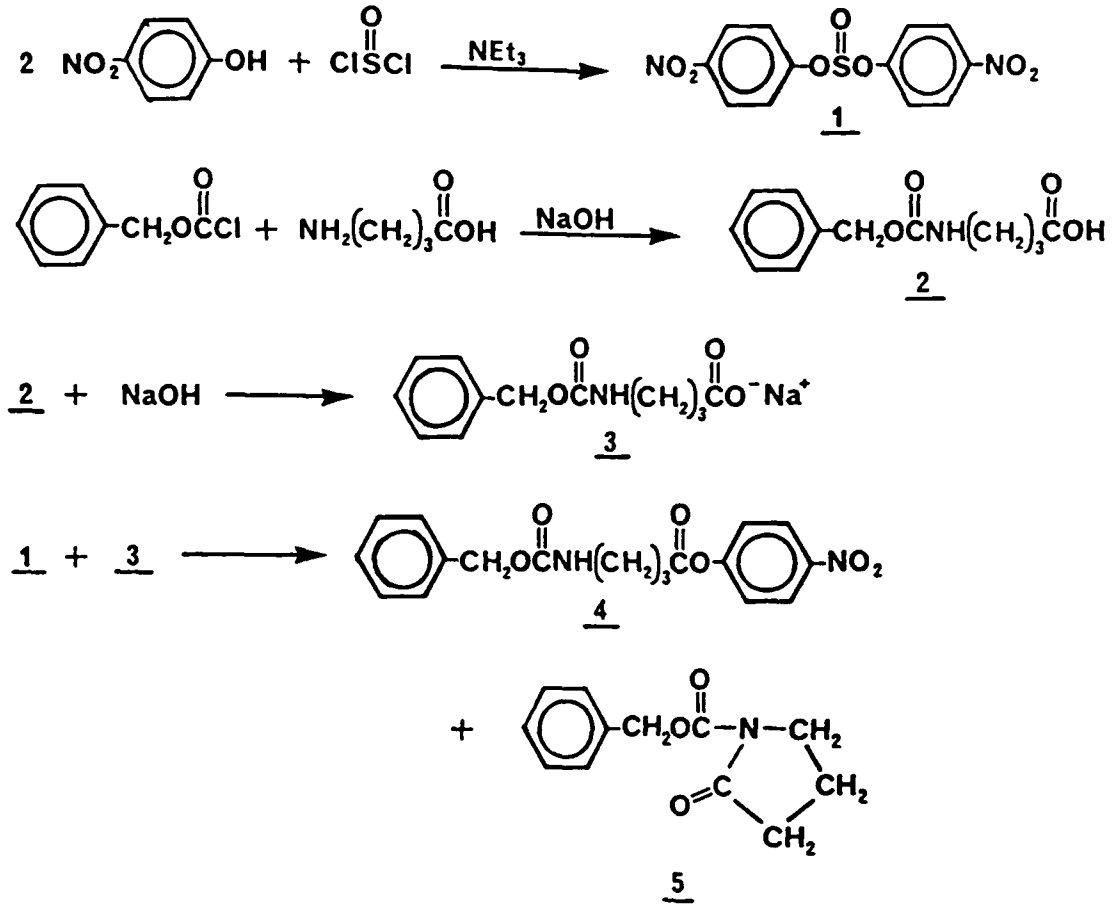
Novel fluoroaliphatic diamines of the type $NH_2CH_2CH_2(CF_2)_nCH_2CH_2NH_2$ (6: n=4, 6a; n=8, 6b) have the potential for being interesting monomers for developing a wide range of new fluoropolymers.

In practice, the process of substituting a fluorodiamine such as 6 for a normal (i.e. nonfluorinated) aliphatic diamine when synthesizing a polymer is not straightforward. Fluoro and normal amines differ in a number of properties [1]. For polymer syntheses the most important difference lies in their reactivity, which is proportional to the basicity. Due to the inductive effect of the fluorine atoms diamines of type 6 are lower in basicity than nonfluorinated aliphatic diamines by a factor of about 100 [2]. When one attempts to synthesize a polymer this reactivity difference can translate into unreasonably long reaction times, low molecular weights, and undesired side reactions.

Peptide blocking group and coupling techniques have been used to synthesize dihydrobromide salts of reactive diamines which contain the fluoroaliphatic moiety (6) [3]. In this paper we report an improved synthetic route to these salts as well as the synthesis and characterization of the free reactive fluoroaliphatic diamines.

RESULTS AND DISCUSSION

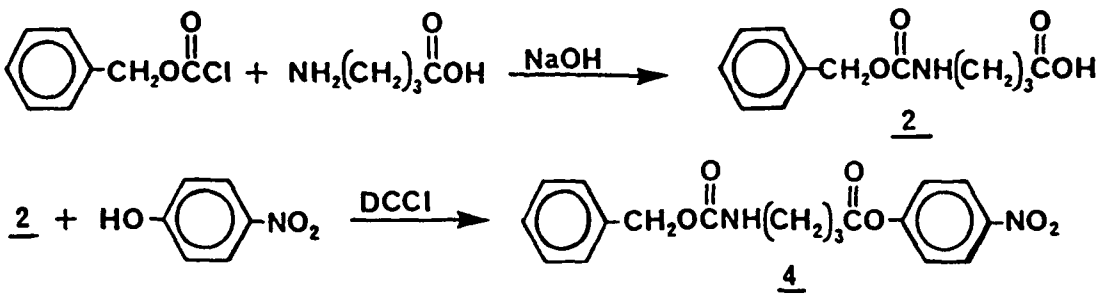
The key step in synthesizing the reactive fluorodiamines (8) and their dihydrobromide salts (9) is the coupling of p-nitrophenyl N-carbobenzoxy-4-aminobutyrate (4) with the fluorinated diamines (6) (see Scheme 3). The previously reported route to synthesizing 4 is outlined in Scheme 1 [3].



Scheme 1

The disadvantages to this approach are the number of steps needed to get to 4 (four), the low yield of 4 (36%), and the formation of the cyclic side product N-carbobenzoxy-2-pyrrolidinone (5) in significant amounts (up to 40%).

We have devised an alternative approach to synthesizing 4 which avoids all of the abovementioned problems, and it is outlined in Scheme 2.



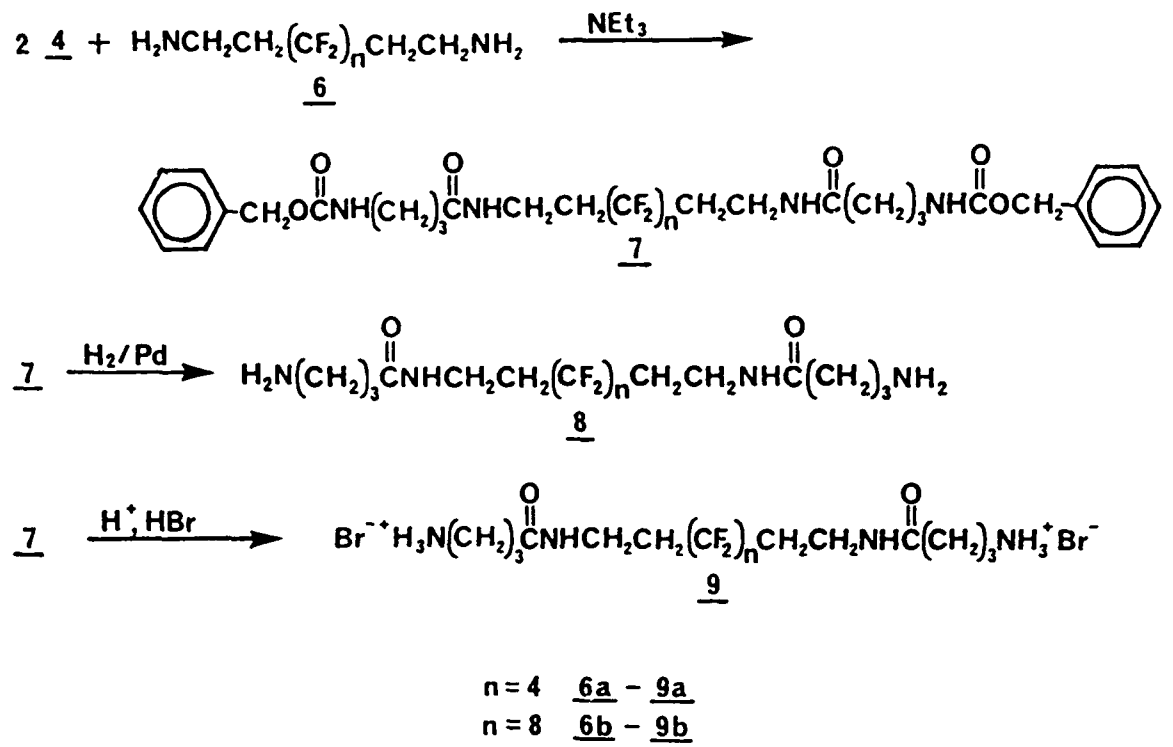
Scheme 2

Coupling of p-nitrophenol with N-carbobenzoxy-4-aminobutyric acid (2) using dicyclohexylcarbodiimide (DCCI) [4] provides a quick, easy, two-step route to obtaining 4 in high yields (80%). The coupling reaction has been successfully run in both methylene chloride and chloroform - methylene chloride is the solvent of choice due to its lower boiling point (i.e. ease of removal). The reaction can be worked up by washing with dilute (5%) sodium bicarbonate solution and water to remove unreacted material; however, this procedure has no significant effect on final product yield or purity, thus rendering it unnecessary.

Despite their lower reactivity the fluorodiamines 6 react well with the p-nitrophenyl "active" ester 4 to give di-N-carbobenzoxy blocked diamines (7) in good yields, as shown in Scheme 3. We have previously demonstrated that the carbobenzoxy groups are easily removed by acidic HBr to give the dihydrobromide salts of the diamines (9) [3]. We now show that the free diamines can be synthesized directly from 7 via hydrogenation over palladium black which, in peptide chemistry, is a well-known technique for removal of N-carbobenzoxy blocking groups [5]. The reaction proceeds cleanly to give quantitative yields of pure diamines (8).

These diamines are solids with moderate melting points, which makes the compounds easy to handle. They are stable but, for long-term storage, they should be kept under either vacuum or an inert atmosphere to avoid carbonate formation.

The reactive diamines 8 differ from the parent diamines 6 in their solubility, most notably in water. 8a is totally water soluble and 8b is partly soluble, whereas 6a is only partly water soluble and 6b is insoluble.



n = 4 6a – 9a
n = 8 6b – 9b

Scheme 3

Preliminary studies involving reactivity show that the diamines derived from neutralization of the dihydrobromide salts (9) undergo interfacial polymerization with diacid chlorides in the same manner as normal aliphatic diamines, whereas attempts with 6 lead to no high molecular weight polymer formation [3]. Thus these new reactive fluorodiamines show promise for being new monomers for making a wide range of novel fluoropolymers. We are investigating their use both in the synthesis of fluoropolyamides and as compatible curing agents for fluoroepoxies.

EXPERIMENTAL

Fluoroaliphatic diamines (6a, 6b) (obtained from Fluorochem, Inc.) and all reagents were used as received. Solvents were dried and purified by standard methods [6,7]. Palladium black catalyst was prepared as described in the literature [5].

Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EMS 390

spectrometer; chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS).

N-carbobenzoxy-4-aminobutyric acid (2)

In a 500 ml erlenmeyer flask equipped with a stir bar was placed 10.30 g (100 mmol) 4-aminobutyric acid, 25 ml 4N NaOH (100 mmol), and 100 ml water. The solution was cooled in an ice bath and, with stirring, to it was added a total of 30 ml 4N NaOH (120 mmol) and 16.55 ml (110 mmol) 95% carbobenzoxy chloride, alternately, in five equal portions over 30 min. Caution was taken to insure that the reaction mixture was kept on the alkaline side at all times, with additional alkali used if necessary. Upon completion of the reaction the solution was extracted once with ether to remove excess acid chloride, then a stream of air was blown over the aqueous phase for 20-30 min to remove residual ether. The solution was transferred into a 1000 ml erlenmeyer flask and water added to give a total volume of 700 ml. With stirring and cooling in an ice bath the solution was slowly acidified with concentrated HCl, during which time the product precipitated. After further cooling and stirring for 30 min in the ice bath (to insure complete precipitation) the crystalline product was collected via filtration and dried to give 22.92 g (97% recovered yield) of 2, mp 68°C. NMR (in $CDCl_3/d_6DMSO$): 11.7 ppm, vbrs, 1H; 7.4 ppm, s, 5H; 6.9 ppm, brs, 1H; 5.1 ppm, s, 2H; 3.2 ppm, q, 2H; 2.3 ppm, tr, 2H; 1.8 ppm, m, 2H.

p-nitrophenyl N-carbobenzoxy-4-aminobutyrate (4)

In a 200 ml round bottom flask equipped with a stir bar was placed 4.74 g (20 mmol) 2, 3.34 g (24 mmol) p-nitrophenol, 4.12 g (20 mmol) DCCI, and 80 ml methylene chloride. The reaction was allowed to proceed with stirring under nitrogen at room temperature overnight. Upon completion the N,N'-dicyclohexylurea which precipitated out of solution during the reaction was filtered off and washed with methylene chloride. The filtrate and washings were combined and the solvent removed via rotary evaporation. The crude crystalline residue was recrystallized from ether/petroleum ether (2/1 v/v) to give 5.76 g (80% recovered yield) of 4, mp 90°C. NMR (in $CDCl_3$): 8.3 ppm, d, 2H; 7.4 ppm, s, 5H; 7.3 ppm, d, 2H; 5.2 ppm, s, 2H; 5.0 ppm, brs, 1H; 3.4 ppm, q, 2H; 2.7 ppm, tr, 2H; 1.9 ppm, m, 2H.

1,8-bis(N-carbobenzoxy-4-aminobutyryl)-3,3,4,4,5,5,6,6-octafluorooctanediamine (7a)

In a 300 ml round bottom flask equipped with a stir bar and a drying

tube was placed 5.10 g (14.3 mmol) 4 and 50 ml chloroform. With stirring and heating to 40°C, a solution of 2.00 g (6.9 mmol) 6a in 50 ml methanol was slowly dripped into the flask. Next a solution of 2.0 ml (14.4 mmol) triethylamine in 20 ml chloroform was slowly added dropwise, with continued stirring and heating. A reflux condenser was placed on the flask, the temperature was raised to 60°C, and the reaction stirred overnight. Upon completion the reaction mixture was slowly cooled to 0°C, during which time the product crystallized out of solution. The product was collected via filtration, washed with cold methanol, dried, and recrystallized from methanol/chloroform (7/1 v/v) to give 2.47 g (49% recovered yield) of 7a, mp 174°C. NMR (in d_6DMSO): 8.1 ppm, brs, 2H; 7.4 ppm, s, 10H; 7.3 ppm, brs, 2H; 5.1 ppm, s, 4H; 3.4 ppm, q, 4H; 3.0 ppm, q, 4H; 2.5 ppm, brm, 4H; 2.1 ppm, tr, 4H; 1.6 ppm, m, 4H.

1,12-bis(N-carbobenzoxy-4-aminobutyryl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecanediamine (7b)

This compound was synthesized in the same manner as 7a, using 3.34 g (9.3 mmol) 4, 2.22 g (4.5 mmol) 6b, and 1.35 ml (9.7 mmol) triethylamine to give, after recrystallization from methanol/chloroform (10/1 v/v), 1.74 g (41% recovered yield) of 7b, mp 170°C. NMR (in d_6DMSO): 8.1 ppm, brs, 2H; 7.4 ppm, s, 10H; 7.3 ppm, brs, 2H; 5.1 ppm, s, 4H; 3.3 ppm, q, 4H; 3.0 ppm, q, 4H; 2.5 ppm, brm, 4H; 2.1 ppm, tr, 4H; 1.6 ppm, m, 4H.

1,8-bis(4-aminobutyryl)-3,3,4,4,5,5,6,6-octafluorooctanediamine (8a)

In a 170 ml tubular reaction vessel equipped with a stir bar was placed an aqueous suspension containing approximately 0.2 g palladium black catalyst. The catalyst was washed several times with ethanol by decantation. To the flask was then added a warm solution (heat necessary for complete solubility) of 1.40 g (1.93 mmol) 7a in 50 ml ethanol. The reaction vessel was fitted with a sealed glass top containing gas inlet and outlet tubes. The inlet tube was positioned below the liquid level in order to bubble hydrogen through the solution. The outlet tube, lying above the liquid level, was connected to a removable bubbler. After purging the system for a few minutes with hydrogen stirring was commenced, a moderate flow of hydrogen was maintained, and the solution was heated to 60°C. The effluent gasses were tested for carbon dioxide by periodic passage through the bubbler containing a saturated barium hydroxide solution. The formation of a white precipitate of barium carbonate within 15 min signalled the onset of reaction. Comparable testing was performed every 20-30 min until completion of the reaction, as indicated by cessation

of carbon dioxide evolution. The total reaction time was 3 hr. The catalyst was then removed from the reaction mixture via filtration and washed with ethanol. The filtrate and washings were combined and the solvent removed via rotary evaporation. Total solvent removal and drying were accomplished by placing the sample under vacuum over P_2O_5 for 24 hr to give 0.88 g (100% recovered yield) of 8a, mp 103°C. NMR (in $CDCl_3/d_6DMSO$): 7.5 ppm, brs, 2H; 3.5 ppm, q, 4H; 2.7 ppm, tr, 4H; 2.5 ppm, brm, 4H; 2.2 ppm, tr, 4H; 1.7 ppm, m, 4H; 1.6 ppm, s, 4H.

1,12-bis(4-aminobutyryl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecanediamine (8b)

This compound was synthesized in the same manner as 8a, using an aqueous suspension containing approximately 0.2 g palladium black catalyst, 1.52 g (1.64 mmol) 7b, and 50 ml ethanol to give 1.08 g (100% recovered yield) of 8b, mp 106°C. NMR (in d_6DMSO): 8.0 ppm, brs, 2H; 3.3 ppm, q, 4H; 2.5 ppm, tr, 4H; 2.4 ppm, brm, 4H; 2.2 ppm, s, 4H; 2.0 ppm, tr, 4H; 1.5 ppm, m, 4H.

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