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Brief 71-10300

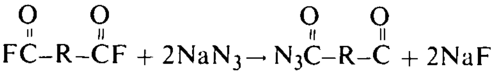
NASA TECH BRIEF

Marshall Space Flight Center

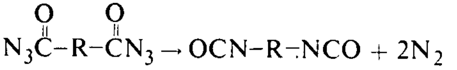
Synthesis of a New Class of Highly Fluorinated Aliphatic Diisocyanates

A laboratory process has been developed for the synthesis of a new class of highly fluorinated aliphatic diisocyanates to be used as a basis for the preparation of polyurethanes that would be compatible with liquid oxygen. Polyurethanes are normally produced from the aromatic toluene diisocyanate, with and without fluorocarbon or other halocarbon moieties, by reaction with various polyols. Although there are a number of commercially available aromatic diisocyanates containing large proportions of fluorine to render them resistant to oxidation, polyurethanes produced from these compounds generally have poor mechanical properties (flexibility, elasticity, tensile strength) at very low temperatures. The polyurethanes prepared by reacting the newly developed fluorinated aliphatic diisocyanates with fluorinated polyols, however, are expected to have outstanding resistance to attack by strong oxidizing agents (e.g., liquid oxygen) and improved mechanical properties at temperatures in the cryogenic region. Members of the fluorinated aliphatic polyurethanes should be curable by conventional methods because the reactive, aliphatic urethane linkage is retained in the "backbone" of the polymer molecule.

The preparation of the fluorinated aliphatic diisocyanates from fluorocarbon diacid fluorides consists of a two-step process, indicated by the following equations in which R denotes a fluorinated aliphatic radical:



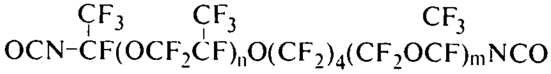
$$F\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}F + 2NaN_3 \rightarrow N_3\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}} + 2NaF \tag{1}$$



$$N_3\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}N_3 \rightarrow OCN-R-NCO + 2N_2 \tag{2}$$

In the first step, carried out at room temperature, a solution of 0.1 mol of a fluorocarbon diacid fluoride in 37 cc of $CF_2Cl\text{-}CFCl_2$ is added dropwise, over a period of two hours, to a suspension of 0.24 mol (0.04 mol in excess of the stoichiometric amount) of activated sodium azide (NaN_3) (see Reference) in 75 cc of dry acetonitrile. After being stirred for an additional two hours, the reaction mixture is washed free of salts, using a 5% aqueous $NaHCO_3$ solution, and is then dried over anhydrous $MgSO_4$.

In the second step, the solution resulting from completion of the first step is slowly stirred into a distillation flask containing 100 cc of near-boiling toluene. The lower-boiling solvents are distilled off, the azide is allowed to decompose exothermally, and nitrogen is evolved. When the exothermic reaction subsides, the mixture is distilled free of acetonitrile and $CF_2Cl\text{-}CFCl_2$ and then refluxed for two hours in order to ensure complete conversion of the acyl azide ($N_3\overset{O}{\overset{\|}{C}}-$) groups to isocyanate (OCN–) groups. The distillate is recombined with the residue in the reflux flask and then fractionated to give the diisocyanate products, in approximately 30 to 60% yield, based on the starting fluorocarbon diacid fluoride. A 58% yield of a specific diisocyanate fraction obtained by this method is represented by the following formula:



$$OCN-\overset{CF_3}{\overset{|}{C}}F(OCF_2\overset{CF_3}{\overset{|}{C}}F)_nO(CF_2)_4(CF_2OCF)_mNCO$$

where m + n = 2.

The identity of each of the diisocyanate fractions was established by infrared analysis, nuclear magnetic resonance, molecular weight, and elemental analysis.

Reference:

Smith, P.A.S.; Organic Reactions. John Wiley & Sons, New York, 1946 (p. 382)

(continued overleaf)

Notes:

1. The novelty of this method lies particularly in the choice of acetonitrile as a solvent in step 1. Its polar nature promotes the indicated ionic reaction; its aprotic property minimizes side reactions; and its volatility facilitates subsequent removal by distillation.
2. Because of inefficiencies inherent in the small-scale experimentation, the yields obtained were not optimum. Considerably larger yields of the diisocyanates would be attainable in controlled large-scale production.
3. Requests for further information may be directed to:

   Technology Utilization Officer
   Code A&TS-TU
   Marshall Space Flight Center
   Huntsville, Alabama 35812
   Reference: B71-10300

Patent status:

Inquiries about obtaining rights for the commercial use of this invention may be made to:

Patent Counsel
Mail Code A&TS-PAT
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

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