Part IV

Synthesis of Pentafluoro-2-azapropene

F. S. FAWCETT, C. W. TULLOCK, and D. D. COFFMAN
Central Research Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

$CF_3N{=}CF_2$ is prepared by the three-step route:

$$ClCN + HF \rightarrow (CF_3)_2NH \rightarrow (CF_3)_2NCF{=}NCF_3 \rightarrow CF_3N{=}CF_2$$

THE FOLLOWING METHOD was the most convenient one for the reasonably large-scale preparation of pentafluoro-2-azapropene. The literature contains several references dealing with the preparation of pentafluoro-2-azapropene (*1–5, 7–9*).

Cyanogen chloride and hydrogen fluoride at 250° C. under autogenous pressure give *N,N*-bis(trifluoromethyl)amine in about 25 to 30% conversion (*6*). The latter with potassium fluoride at 200° C. gives the dimer in 80% conversion which by flow pyrolysis over sodium fluoride pellets at 525° C. yields pentafluoro-2-azapropene in 84% conversion. Direct removal of hydrogen fluoride from the amine to form the azapropene is complicated by partial dimerization of the latter by fluoride agents (*1–5, 7–9*) employed to sequester the hydrogen fluoride, but the reaction can be directed to the formation of the dimer in high conversion. Conversion of dimer to monomer was examined on an analytical scale by use of a pyrolysis–gas chromatography (GC) procedure in which the pyrolysate from a small reactor was led directly into a GC column. Products were identified by trapping for infrared or mass spectral analysis. Metal fluoride catalysis is illustrated by the following data at about 7 seconds contact time: over nickel gauze at 500° to 600° C., about 30% conversion; over cesium fluoride at 355° C., 90% conversion.

N,N-BIS(TRIFLUOROMETHYL)AMINE

A mixture of 61 grams of cyanogen chloride (from American Cyanamid Co.) and 100 grams of anhydrous hydrogen fluoride in a 1-l. Hastelloy C reactor was heated under autogenous pressure with rocking at 75° C. for 3 hours, at 150° C. for 1 hour and 250° C. for 6 hours. After cooling, the contents of the reactor were passed through a tower containing ⅛-inch sodium fluoride pellets (from Harshaw Chemical Co.), and the product was collected in a second metal vessel containing 250 grams of ⅛-inch sodium fluoride pellets to absorb hydrogen halides. Eight such runs were made, reloading the reactor without opening between runs. The combined volatile product was stored over the sodium fluoride at room temperature and autogenous pressure for at least 24 hours and then distilled through a glass helix-packed column to obtain 141 grams of *N,N*-bis(trifluoromethyl)amine, b.p. −8° to −6° C.

PENTAFLUORO-2-AZAPROPENE DIMER

A mixture of 110 grams of *N,N*-bis(trifluoromethyl)amine and 120 grams of anhydrous potassium fluoride in a 500-ml. Hastelloy reactor was heated with rocking under autogenous pressure at 200° C. for 6 hours. Two combined runs gave 154 grams (80% conversion) of the dimer, $(CF_3)_2NCF{=}NCF_3$, b.p. 33° to 36° C.

PENTAFLUORO-2-AZAPROPENE BY PYROLYSIS OF DIMER

A ¾-inch I.D. nickel tube containing 90 grams of ⅛-inch sodium fluoride pellets was preheated to 700° C. in a stream of nitrogen and then, at 525° to 530° C., 194 grams of the dimer was introduced at atmospheric pressure during 8.5 hours while the evolved product was collected in cold traps. Distillation gave 163 grams (84% conversion) of pentafluoro-2-azapropene, b.p. −28° to −25° C.

ACKNOWLEDGMENT

The authors are indebted to J. Q. Townley for the pyrolysis–gas chromatography apparatus (similar in design to that previously used in this laboratory by E. P. Blanchard) and for carrying out the experiments and to H. E. Cuprey for improvements in the procedure for synthesizing *N,N*-bis(trifluoromethyl)amine.

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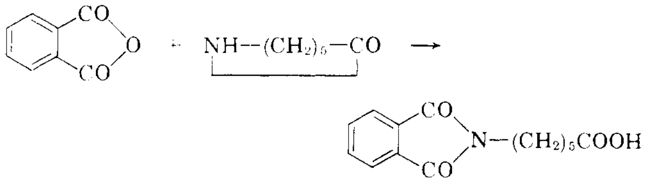
ε-Imido Esters. The Reaction Between Anhydrides and ε-Caprolactam

BERNARD TAUB and HANS A. LEIPOLD[1]
National Aniline Division, Allied Chemical Corp., Buffalo, N. Y.

ε-Caprolactam reacts with cyclic anhydrides to yield the corresponding ε-imidocaproic acids which are converted to esters by normal esterification methods. ε-Imidocaproic acid esters, of the open-chain variety are prepared by condensing an acyclic anhydride with alkyl-6-isocyanatocaproates.

As previously shown (5), phthalic anhydride reacts with ε-caprolactam at elevated temperatures to yield ε-phthalimidocaproic acid instead of the expected corresponding *N*-acyl-ε-caprolactam derivative.



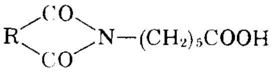
The utility of the esters of ε-phthalimidocaproic acid as plasticizers for both poly(vinyl chloride) and nylon molding resins, prompted an extension of the authors' investigation of the reaction between anhydrides and ε-caprolactam to include both cyclic and acyclic anhydrides.

ε-Caprolactam was condensed with a variety of cyclic anhydrides (phthalic, hexahydrophthalic, tetrahydrophthalic, succinic, and dodecenylsuccinic anhydrides) to yield the corresponding ε-imidocaproic acids. The physical properties of the compounds are summarized in Table I. Attempts to prepare the ε-imidocaproic acid from maleic anhydride and ε-caprolactam resulted in the formation of polymeric products.

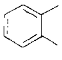
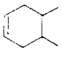
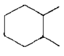
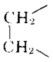
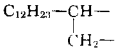
The ε-imidocaproic acids from the cyclic anhydrides were converted to esters by interaction with a variety of alcohols using conventional esterifying techniques. Table II lists the physical properties of the ε-imidocaproic acid esters.

The synthesis of ε-imidocaproic acids in which the imide structure is of the open-chain variety, could not be accomplished using the aforementioned technique. Thus, when ε-caprolactam was condensed with an acyclic anhydride—

Table I. ε-Imidocaproic Acids



$$R{<}^{CO}_{CO}{>}N-(CH_2)_5COOH$$

R	Yield, %	M.P., ° C.[a]	B.P., ° C./Mm. Hg	Neut. Equiv. Calcd.	Neut. Equiv. Found	Nitrogen, % Calcd.	Nitrogen, % Found
	70	107-108	239-240/3	261	265	5.4	5.5
	86	80	221-224/1	265	265	5.1	5.3
	62	. . .	235-239/3	267	271	5.2	4.9
 CH_2- / CH_2-	52	82-84	216-220/2	213	215	6.6	6.5
 $C_{12}H_{23}-CH(-)-CH_2-$	28	. . .	247-252/2	379	384	3.7	3.6

[a] Melting points are uncorrected.

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[1] Present address: Sinclair Oil Co., Chicago, Ill.