bonds. The possibility that linkages other than disulfide bonds are involved has not been excluded.

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THE HOMOPOLYMERIZATION OF MONOISOCYANATES

Sir:

Beyond the formation of cyclic dimers[1] and trimers[2] from monoisocyanates (Reactions I and II in Fig. 1) and the suggestion that cyamelide[3] is a linear polyisocyanic acid, there has been no evidence to indicate the possibility of obtaining addition polymers from monofunctional compounds containing $>C{=}N-$ groups. I have recently found that monoisocyanates can be polymerized to linear high molecular weight polymers in a manner similar to vinyl compounds in accordance with the Reaction III in Fig. 1. These polymers may be regarded as N-substituted "1-nylons."

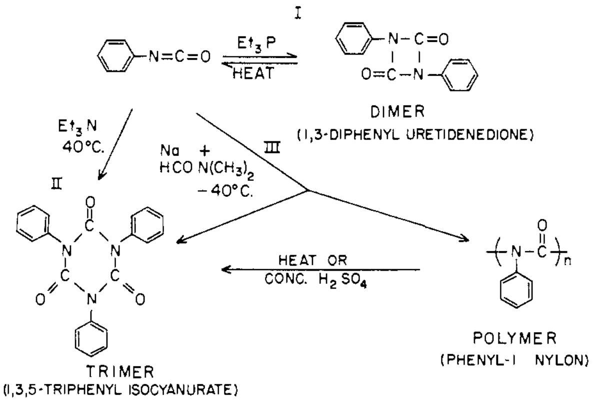

Fig. 1.—Reactions of phenyl isocyanate.

The polymerization takes place at low temperatures (−20° to −100°) in polar solvents, such as N,N-dimethylformamide, N,N-dimethylacetamide and triethylamine, through the use of anionic initiators. Ethyl isocyanate and phenyl isocyanate, examples of an aliphatic and aromatic isocyanate, were polymerized in the manner to be described.

Ethyl isocyanate, 25 ml., and dry triethylamine, 25 ml., both previously cooled to −40°, were stirred together rapidly under dry nitrogen, and further cooled to −100° with liquid nitrogen. Next 10 ml. of a sodium catalyst solution in N,N-dimethylformamide[4] was added to the rapidly stirring solution during about 30 seconds. A white, fibrous solid precipitated immediately upon contact of the catalyst with the monomer solution. The solid was filtered off, washed with methanol and dried to give 8.5 g. (39%) of ethyl 1-Nylon polymer (m.p. 250° with decomposition; found: C, 50.76; H, 6.88; N, 19.34). From the filtrate the cyclic trimer, 1,3,5-triethyl isocyanurate, was isolated and identified by its solubility and melting (m.p. 94°) characteristics.

Ethyl 1-Nylon was soluble in trifluoroacetic acid (TFA) and concentrated sulfuric acid. Clear films were obtained when TFA solutions were air dried and extracted with methanol at room temperature. Prolonged standing of the polymer in TFA resulted in degradation: a change in the inherent viscosity at 0.5% concentration from 0.3 to 0.04 occurred in two days. Light scattering studies on the aged solution gave a molecular weight value of 1600–3000 (*i.e.*, a D.P. of 23 to 42).[5] The polymer was further characterized by its distinct infrared spectrum where the only significant bands were those corresponding to carbonyl at 5.85μ, N,N-disubstituted amide at 7.4μ and a conspicuous absence of isocyanate and NH bands.[5]

With phenyl isocyanate, a polymer (m.p. 197° with decomposition) was obtained in 86% yield in N,N-dimethylformamide using the sodium catalyst[4a] at −40°. The polymer was soluble in concentrated sulfuric acid, but insoluble in TFA and chlorinated hydrocarbons. Its infrared spectrum was consistent with a phenyl 1-Nylon structure and quite distinct from either the dimer or trimer of phenyl isocyanate.

[1] A. W. Hofmann, *Ber.*, **3**, 765 (1870).

[2] D. H. Chadwick and T. C. Allen, U. S. Patent 2,733,254 (1956).

[3] W. Kern, H. Paul and W. Mehren, *Makromol. Chem.*, **14**, 146 (1954).

[4] (a) The catalyst solution was prepared by adding 10 drops of a 50% sodium dispersion in xylene (du Pont Electrochemicals Department) to 50 ml. of dry N,N-dimethylformamide. The mixture was stirred for 1 hour before use. (b) The use of this combination as a catalyst for the anionic polymerization for vinyl compounds was demonstrated by L. Grandine, E. I. du Pont de Nemours & Company (private communication).

[5] The author wishes to thank Drs. D. Akeley and R. Zbinden for the light scattering data and infrared analysis, respectively.

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STEROIDS. CXXII.[1] 6α-FLUORO-16α-METHYLCORTICOIDS—SYNTHESIS AND BIOLOGICAL ACTIVITY

Sir:

Among the most recent chemical modifications of the hydrocortisone and prednisolone molecule—resulting in increased anti-inflammatory activity and diminution of salt retention—have been introduction of a 6α-fluorine atom[1,2,3] *or* addition of a methyl group in the 16α-position.[4,5] We now wish to report the synthesis and preliminary biological evaluation of analogs of the most important cortical hormones combining *both* of these structural features.

The preparation in this Laboratory of 6α-fluoro-16α-methylhydrocortisone acetate (I) *via* 6α-fluoro-16α-methyl "Substance S" already has been recorded.[6] Dehydration of I with mesyl chloride in

[1] Paper CXXI, A. Bowers, E. Denot, M. B. Sánchez and H. J. Ringold, *Tetrahedron*, in press.

[2] A. Bowers and H. J. Ringold, THIS JOURNAL, **80**, 4423 (1958).

[3] J. A. Hogg, G. B. Spero, J. L. Thompson, B. J. Magerlein, W. P. Schneider, D. H. Peterson, O. K. Sebek, H. C. Murray, J. C. Babcock, R. L. Pederson and J. A. Campbell, *Chemistry and Industry*, 1002 (1958).

[4] G. E. Arth, J. Fried, D. B. R. Johnston, D. R. Hoff, L. H. Sarett, R. H. Silber, H. C. Stoerk and C. A. Winter, THIS JOURNAL, **80**, 3161 (1958).

[5] E. P. Oliveto, R. Rausser, L. Weber, A. L. Nussbaum, W. Gebert, C. T. Coniglio, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman and M. M. Pechet, *ibid.*, **80**, 4431 (1958).

[6] J. A. Edwards, A. Zaffaroni, H. J. Ringold and C. Djerassi, *Proc. Chem. Soc.*, 87 (1959). All intermediates in that synthesis were