dione by a mixture of ethoxyacetylene, DMSO, pyridine, and orthophosphoric acid.

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*Received August 12, 1965*

Synthesis of High Polymeric Alkoxy- and Aryloxyphosphonitriles

Sir:

High molecular weight phosphonitrilic halide polymers (polydichlorophosphazenes) have received wide attention in recent years because they are elastomeric and do not decompose thermally below 300°; they are, however, extremely susceptible to hydrolytic degradation. This sensitivity to moisture is due principally to hydrolysis of the phosphorus–halogen bonds. Many attempts have been made to prepare linear, high molecular weight organophosphonitrile polymers in the belief that total replacement of the halogen atoms by organic groups would reduce or eliminate the hydrolytic instability. Thus, polymeric bis(trifluoromethyl)phosphonitrile, $[NP(CF_3)_2]_n$, and diphenylphosphonitrile, $[NP(C_6H_5)_2]_n$, were synthesized by Tesi, Haber, and Douglas,[1] by Tesi and Douglas,[2] and by Herring[3] from bis(trifluoromethyl)phosphinic azide,[1] bis(trifluoromethyl)phosphinous amide,[2] and from diphenylchlorophosphine,[3] respectively. These polymers were hydrolytically stable, and the trifluoromethyl derivative was thermally stable up to 380°.[4] However, these materials were not fully characterized, and no information was reported concerning the molecular weights or the detailed molecular structure. Attempts have also been made to prepare polymeric alkoxyphosphonitriles by the direct replacement of halogen in phosphonitrilic chloride rubber by alkoxyl groups.[5,6] These attempts did not yield linear polymers. Goldschmidt and Dishon[5] obtained cross-linked, partially substituted products using alcohol-pyridine or sodium alkoxide reagents, and Lenton, Lewis, and Pearce[6] recently reported similar results when swelled phosphonitrilic chloride rubber was treated with ethanol-pyridine or trifluoroethanol-pyridine reagents. The trifluoroethoxy polymer was not stable above 200°.

We now wish to report the synthesis of the first examples of soluble, uncross-linked, fully substituted, high molecular weight organophosphonitrile polymers. The method used involved the polymerization of phosphonitrilic chloride trimer (hexachlorocyclotriphos-

phazene), $(NPCl_2)_3$, to a mixture of *soluble*, high polymers, $(NPCl_2)_n$, in which n ranged from 3 to over 15,000. The higher molecular weight, soluble polymer appears to be an open-chain precursor of the cross-linked material which is commonly described as "phosphonitrilic chloride rubber." The soluble polymer can be obtained by termination of the polymerization at a stage before cross-linking occurs. This mixture of soluble chlorophosphonitrile polymers was then allowed to react with sodium alkoxide or phenoxide to give a mixture of fully substituted organophosphonitrile polymers

$$(NPCl_2)_n + 2nNaOR \longrightarrow [NP(OR)_2]_n + 2nNaCl$$
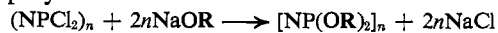
from which the higher homologs could be isolated by fractional precipitation. The following example illustrates one of the experimental procedures employed.

Phosphonitrilic chloride trimer (200 g.) was polymerized under vacuum for 4 hr. at 250°.[7] The mixture of phosphonitrilic chloride polymers (1.725 moles of $NPCl_2$) was then dissolved in dry benzene (1000 ml.) and was treated with a solution of sodium trifluoroethoxide (3.45 moles) in diethyl ether (1500 ml.) for 28 hr. at 57°. The mixture was then neutralized to litmus with concentrated hydrochloric acid, and the precipitate was filtered off, washed with methanol and with water, and dried. This product was a mixture of fully substituted oligomers and polymers. The high polymers were obtained by fractional precipitation of an acetone solution of the products into benzene to give poly[bis(trifluoroethoxy)phosphonitrile] (55 g.).

Anal. Calcd. for $C_4H_4F_6NO_2P$: C, 19.77; H, 1.66; F, 46.9; N, 5.76; P, 12.74. Found: C, 20.28; H, 1.95; F, 47.21; N, 5.73; P, 12.99; Cl, 0.

The number-average molecular weight was found by osmotic pressure to be 90,000; the weight-average molecular weight was found by light scattering in ethyl trifluoroacetate to be 1,700,000 ($\pm$ 500,000); and the intrinsic viscosity of the polymer in acetone at 30° was 1.92 dl./g. An infrared spectrum showed a P=N stretching peak as part of a multiple band in the 1270 cm.$^{-1}$ region, and ^{31}P n.m.r. spectra showed a single peak at $+7.5$ p.p.m., both of these values being consistent with a linear, fully substituted structure (I).

I
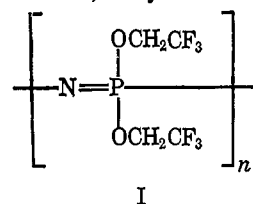
The polymer was soluble in acetone, tetrahydrofuran, ethyl acetate, ethylene glycol dimethyl ether, and methyl ethyl ketone, but insoluble in many other organic liquids. It was completely stable to water. The polymer was crystalline over a wide temperature range, with a glass transition temperature (determined by differential thermal analysis) of $-66°$ and a crystalline melting temperature (determined by optical birefringence) in the 240° region. The chain repeating distance of 4.81 Å., measured by X-ray diffraction, is close to the value of 4.92 Å. reported for $(NPCl_2)_n$.[8]

(1) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).
(2) G. Tesi and C. M. Douglas, *J. Am. Chem. Soc.*, 84, 549 (1962).
(3) D. L. Herring, *Chem. Ind.* (London), 717 (1960).
(4) C. P. Haber, Inorganic Polymers, International Symposium, Nottingham, July 18–21, 1961, Special Publication No. 15, The Chemical Society, London, p. 119.
(5) F. Goldschmidt and B. Dishon, *J. Polymer Sci.*, 3, 481 (1948).
(6) M. V. Lenton, B. Lewis, and C. A. Pearce, *Chem. Ind.* (London), 1387 (1964).

(7) The rate of polymerization varies enormously with the presence of trace impurities. Polymerization times up to 48 hr. were sometimes required in order to achieve satisfactory conversions to soluble polymer.
(8) E. Giglio, F. Pompa, and A. Ripamonti, *J. Polymer Sci.*, 59, 293 (1962).

Thermogravimetric analysis curves showed that the T_{10} weight-loss values (10°/min.) in air and in nitrogen were 405 and 420°, respectively, although the polymer appears to be susceptible to depolymerization below 200°.

The above procedure has also been extended to the synthesis of soluble, high molecular weight dimethoxy-, diethoxy-, and diphenoxypolyphosphonitriles. These polymers were analytically pure, with weight-average molecular weights close to or above 1×10^6 and glass transition temperatures at -76, -94, and $-8°$, respectively. A related procedure has been employed for the synthesis of aminophosphonitrile high polymers of structure $[NP(NRR')_2]_n$. The details of these syntheses will be reported subsequently.

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Halogen Addition to Bicyclo[2.1.0]pentane[1]

Sir:

The course of reaction of bicyclo[2.1.0]pentane with electrophilic reagents is now known to be completely dominated by the maximum release of strain as opposed to the electronic and statistical factors which determine the course of cleavage in less strained bicyclo[n.1.0]alkanes. Reactions of bicyclo[2.1.0]pentane with mercuric,[2a] lead, and thallium acetates[2b] and p-toluenesulfonic acid in acetic acid[2c] give as the only products those which result from the cleavage of the internal carbon–carbon bond. Bicyclopentane is also known to react readily with bromine,[3] but the nature of the product has not been reported. In this communication the unusual mode of bromine and chlorine addition is reported.

The bicyclopentane used was prepared by the method of Criegee[3] and gave a single peak on gas chromatography under conditions (10 ft. $\times$ $^3/_{16}$ in., 5% squalane on firebrick, 30°) by which the presence of 1% cyclopentene could be determined. The dropwise addition of bromine in anhydrous chloroform to bicyclopentane in chloroform was carried out at -30 and $-25°$ in the dark. Careful removal of the solvent by distillation at 0° and reduced pressure gave in 85–90% yield the crude product which was analyzed directly. Surprisingly, the infrared ($\lambda_{max}^{CCl_4}$ 7.62, 7.84, 8.59, 9.59, 9.68, and 11.17 μ) and n.m.r. spectra (doublet of triplets centered at τ 5.30 and complex multiplets in the region of 6.9–8.3) of the product were identical in all respects with the spectra of authentic trans-1,2-dibromocyclopentane. However, gas chromatograms (obtained by using a 3 ft. $\times$ $^3/_{16}$ in. polyethylene glycol adipate on firebrick column at 135°) demonstrated the presence of two additional materials, one of which was present in 7–9% and was identified by its retention time as cyclopentyl bromide. The third component, emerging at a slightly longer retention time than the predominant component, was always present to the extent of 2% or less and remains unidentified.

Addition of chlorine to bicyclopentane in the dark at -25 to $-40°$ in anhydrous chloroform gave a complex mixture of chlorides but, again, the trans-1,2-dihalocyclopentane predominated. Quantitative and preparative scale gas chromatography of the crude product mixture was carried out employing conditions[4] similar to those used by Russell[5] in his chromatographic analysis of the isomeric dichlorocyclopentanes. The following, given in the order of increasing retention time, were the identified products present in the amounts specified: cyclopentyl chloride (5%), trans-1,2-dichlorocyclopentane (62%), trans-1,3-dichlorocyclopentane (8%), and cis-1,3-dichlorocyclopentane (5%). Three unidentified components emerge at retention times much longer than the retention times of any of the five isomeric dichlorocyclopentanes. These three components make up 20% of the product mixture. Cyclopentyl chloride and all the dichlorides were identified by matching the retention times of components of the product mixture with the retention time of authentic materials.[6] The major component was isolated and its identity was confirmed through its n.m.r. and infrared spectra.

The possibility that isomerization of bicyclopentane to cyclopentene takes place under reaction conditions is remote. Bicyclopentane must be heated above 300° ($E_{act} = 45.6$ kcal./mole)[7] to effect isomerization to cyclopentene. Moreover, addition of bromine and chlorine to cyclopentene gave cleanly the trans-1,2-dihalocyclopentanes at a rate which appears to be at least the same if not slower than the addition of halogen to bicyclopentane under precisely the same reaction conditions. The possibility that initially formed, less stable dihalocyclopentanes could be rearranging to trans-1,2-dihalocyclopentanes can be excluded on the basis that trans-1,3-dichlorocyclopentane, cis-1,2-dibromocyclopentane, and trans-1-bromo-3-chlorocyclopentanes all survive the halogen addition conditions.

The predominance of trans-1,2-dihalocyclopentane formation can be explained in terms of the scheme depicted below. The transition state for the initial

1,3-dihalo cyclopentanes   trans-1,2-dihalo cyclopentanes
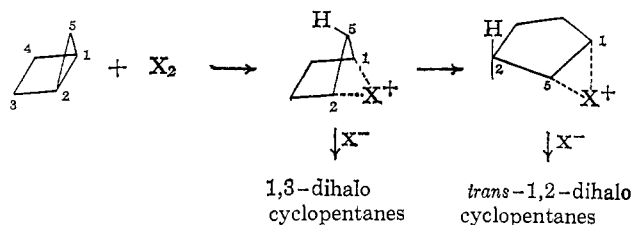
attack of bicyclopentane by electrophilic halogen would closely resemble the highly strained substrate. The resulting 1,3-halonium ion would still possess much of the strain of the substrate in achieving maximum overlap of the orbitals of halogen with the p-rich sp^3 orbitals of C-1 and C-2. Relief of this strain is the driving force for a 1,2-hydride migration which results in the rapid conversion of the 1,3-halonium ion to a

(1) Paper VI in a series entitled Carbon–Carbon Bond Fission in Cyclopropanes.

(2) (a) R. Ya. Levina, B. N. Kostin, and T. K. Ustynyuk, *Zh. Obshch. Khim.*, 30, 359 (1960); (b) R. J. Ouellette, A. South, Jr., and D. L. Shaw, *J. Am. Chem. Soc.*, 87, 2602 (1965); (c) R. T. LaLonde and L. S. Forney, *ibid.*, 85, 3767 (1963).

(3) R. Criegee and R. Rimmelin, *Chem. Ber.*, 90, 414 (1957).

(4) Di(2-ethylhexyl) sebacate (5–7 ft. $\times$ $^3/_{16}$ in., 20%) on Chromosorb P, at 120°.

(5) G. A. Russell and A. Ito, *J. Am. Chem. Soc.*, 85, 2983 (1963).

(6) There can be no doubt about the use of retention times to identify components of the product mixture. The appearance sequence of the five dichlorocyclopentanes has been determined (ref. 5), and similar chromatographic conditions have been employed in the work reported herein.

(7) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, 86, 678 (1964).