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Selected bond lengths (Å) are: Re-Ge = 2.591(3); Ge-O5' = 1.96(2); C5-O5 = 1.27(3); Re-C5 = 2.14(3); av Re-C(1-4) = 1.92(3); av C(1-4)-O(1-4) = 1.15 (3). Selected bond angles (deg) are: Re-C5-Ge = 111 (2); Re-C5-O5 = 121 (2); C8-C5-O5 = 128 (2); Ge-O5'-C5' = 139 (2); Ge-Re-C5 = 82.8 (6); Re-Ge-O5' = 107.6 (4).

-25°, thermodynamic parameters for this process were determined to be ΔH° = 6.7 ± 0.3 kcal and ΔS° = 27.9 ± 1.4 eu.8

The 13C nmr spectrum in CDCl3 at −30° confirmed the presence of two distinct species in solution. Particularly noteworthy were two peaks at −337.72 and −335.20 ppm, relative to TMS, which established that both species contained carbene carbon atoms.4

It has not been possible to obtain crystals of 1 suitable for crystallographic study. We therefore prepared the rhenium analog5 for crystallographic study. We therefore prepared the rhenium analog5 for crystallographic study. It has not been possible to obtain satisfactory crystals of it despite its lesser stability in the presence of two distinct species in solution. Par­

The X-ray diffraction study showed that the crystals contained the dimer rather than the monomer.7 The crystals exhibited twinning and the apparent space group and unit cell were determined to be I2/m, a = 9.639(8) Å, b = 11.504(9) Å, c = 11.140(9) Å, and β = 97.22 (1)°. This cell is a composite of two orientations of a triclinic cell with space group P1 and approximate dimensions a ∼ b = 9.05 Å, c = 9.63 Å, α = 106.9°, β = 118.0°, and γ = 101.0°. The density was measured by flotation as 2.37(2) g cm−3.

The mass spectrum of this dimeric species shows only peaks due to the monomeric form. On this basis, the mass spectra of 1 and its diphenyl analog1 which also show only monomer, would be consistent with the four-membered heterocyclic structure earlier proposed1 for the monomeric form of 1 is correct.

The molecule contains an unusual eight-membered, heterocyclic ring of rhenium, germanium, oxygen, and carbon atoms. Selected bond lengths and angles are given in the caption to Figure 1. Of particular interest are the planarity of the carbene carbon atoms and the three attached groups and the rather long germanium–oxygen distance, which may result from the strong interaction between the oxygen and carbene carbon.

The structure provides excellent support for the dimer–monomer equilibrium described above, as well as suggesting that the four-membered heterocyclic structure earlier proposed1 for the monomeric form of 1 is correct.

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Supplementary Material Available. A listing of atom coordinates of [Me2GeRe(CO)4(CO)Me] will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-5931.

(8) Refinement was carried out in I2/m. The space group P1 was also used varying the relative weights of the two components but essentially refined to equal weights, which is the I2/m solution.

(10) See paragraph at end of paper regarding microfilm material.

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Chirality in Polysicyanides

Sir:

It has been suggested1-3 from Stuart models that the backbone of polysicyanides (I) has the conformation of a tightly coiled helix. In particular this would be


the case for polymers of isocyanides with bulky side groups like 1a.

\[
[\text{C}=\text{NR}] R_1 R_2 R_3 \]

1a, \(R_1 = R_2 = R_3 = \text{CH}_3\)

b, \(R_1 = H; R_2 = \text{CH}_3; R_3 = \text{C}_2\text{H}_5\)

c, \(R_1 = H; R_2 = \text{CH}_3; R_3 = \text{C}_2\text{H}_5\)

If the models are realistic, polyisocyanides consist of racemic mixtures of left-handed and right-handed helices. In order to prove the occurrence of enantiomers, we first tried to synthesize the polymers asymmetrically. Polymerization of isocyanides was performed in benzene solution at 25° with (+)-nickel chloride and nickel acetylacetonate in the presence of (−)-borneol. The polymers obtained did not show optical activity. The same negative result was found when the polymerization was carried out in (+)-sec-butyl alcohol as a chiral solvent.

However, a slightly asymmetric reaction was observed when racemic α-phenylethyl isocyanide was polymerized in methanol at 25° with (+)-nickel alamine as a chiral catalyst. The polymer (1b) isolated at different intervals showed a weak negative optical rotation, \([\alpha]_{275} = -0.4° (c \, 2, \text{benzene})

The observed optical activity does not arise from the catalyst which has an opposite sign of rotation. Nevertheless, no definite conclusions can be drawn from this small effect with regard to the secondary structure of polyisocyanides. Moreover, an optical rotation found in 1b is not of necessity connected with helix conformations, because the monomeric isocyanide is a racemic mixture of enantiomers which might give some asymmetric selective polymerization with a chiral catalyst.

A resolution of polyisocyanides by column chromatography on a chiral support appeared to be successful. As supporting materials poly[(+)-sec-butyl isocyanide] and poly[(-)-sec-butyl isocyanide] and (−)-1c, were used. These polymers were synthesized from the corresponding optically active monomers (optical purity 96%) by 0.1 mol % nickel chloride at different intervals showed a weak negative optical rotation, \([\alpha]_{275} = -0.4° (c \, 2, \text{benzene})

With (+)-1c as a supporting polymer a partial resolution has been obtained of poly(tert-butyl isocyanide) (1a), which is soluble in chloroform. A typical example is given in Table I. Reversed signs were obtained after chromatographing a sample of 1a three times over (+)-1c. ORD shows a gradual increase of rotation from 600 to 400 nm by a factor of 6.

Attempts to resolve low molecular weight compounds such as sec-butylamine and sec-butyl alcohol by chromatography over the same supporting material have failed. This suggests that the conformation of the principal chain of the polymers plays an important role in the resolution process of 1a. If the models are realistic, poly(4-methyl-1-hexene), which has chiral atoms in the lateral chain, by using an optically active poly(S-3-methyl-1-pentene) as chromatographic support. As far as we are aware, resolution of polymers, which have chiral centers neither in the principal nor in the lateral chain, has not been reported before.


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Photoisomerization of 2-Pyridylacetonitrile to Anthranilonitrile

Sir:

During the course of our investigations of the photochemical behavior of α-alkylpyridines substituted at the side-chain, 2-pyridylacetonitrile (1) was found to photoisomerize to anthranilonitrile (2) in a good yield. The reaction does not occur in the absence of ultraviolet light.

Preparative-scale photolysis of 1 (3.4 × 10⁻² M) in ethyl ether–tert-buty alcohol, followed by separation by column chromatography (Florisil) led to the isolation of 2 (mp 47–48°) in a yield of 44.3%. The mass spectrometry of the product (M + 118) indicates that this is an isomer of 1. The infrared spectra of the product showed strong bands at 1620, 3350, and 3450 cm⁻¹, suggestive of the aromatic primary amine. The structure of the product was established by comparison with the spectral properties of an authentic sample.

Irradiation of 1 in other solvents also afforded 2 in various yields.


(2) 2-Pyridylacetonitrile (1) was prepared by dehydration of 2-pyridylacetamide; nmr (CCl₄) δ 8.42 (m, 1 H), 7.43 (m, 3 H), 3.84 (s, 2 H); ir (KBr) (cm⁻¹) 3450, 3240 (e 3800); ir (KBr) (cm⁻¹) 3450, 3350, 2200, 745; nmr (CCl₄) δ 7.3–7.4 (m, 4 H), 4.5 (s, 2 H), exchangable with D₂O.


(5) 2-Pyridylacetonitrile (1) was prepared by dehydration of 2-pyridylacetamide; nmr (CCl₄) δ 8.42 (m, 1 H), 7.43 (m, 3 H), 3.84 (s, 2 H); ir (KBr) (cm⁻¹) 3450, 3350, 2200, 745; nmr (CCl₄) δ 7.3–7.4 (m, 4 H), 4.5 (s, 2 H), exchangable with D₂O.

(6) In the solvents shown in Table I, 2 is the major photoproduct accompanied by a trace of some other components by glc analysis (PEG 20M on Chromosil, 2m at 100–250°). In some cases, an appreciable amount of polymeric material was obtained. In colloids bearing an α-hydrogen, e.g., ethanol, another photoproduct was obtained which is probably a 1:1 adduct of 1 with the alcohol.