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

$$[>C{=}NCR^1R^2R^3]_n$$

1a, $R^1 = R^2 = R^3 = CH_3$
b, $R^1 = H$; $R^2 = CH_3$; $R^3 = C_6H_5$
c, $R^1 = H$; $R^2 = CH_3$; $R^3 = C_2H_5$

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° by 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 alaninate as a chiral catalyst. The polymer (**1b**) isolated at different intervals showed a weak negative optical rotation, $[\alpha]^{27}_{578}$ −0.4° (*c* 2, 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], (+)-**1c** and (−)-**1c**, were used. These polymers were synthesized from the corresponding optically active monomers[4] (optical purity 96%) by 0.1 mol % nickel chloride in methanol at 25°. These polymers **1c** are highly insoluble in organic solvents and water; their optical rotation could not be measured.

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 observed when (−)-**1c** was used as supporting material. The highest specific optical rotation measured so far for fractions of **1a** is $[\alpha]^{20}_{578}$ −16°. This result was obtained after chromatographing a sample of **1a** three times over (+)-**1c**. ORD[4] shows a gradual increase of rotation from 600 to 400 nm by a factor of 6.

Table I. Chromatographic Resolution[a] of Poly(*tert*-butyl isocyanide). Supporting Medium Poly[(+)-*sec*-butyl isocyanide][b]

Fraction	Fraction weight/g	$[\alpha]^{20}_{578}$[c]
1	0.094	+5.2°
2	0.066	0.0°
3	0.061	−1.9°
4	0.066	−5.5°

[a] Eluent chloroform, at 25°. [b] Weight of supporting polymer 7 g, weight of supported polymer 0.300 g, total polymer eluted 0.287 g. [c] In chloroform.

Attempts to resolve low molecular weight compounds such as *sec*-butylamine and *sec*-butyl alcohol by chromatographing 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**.[5]

Reports of polymer resolution are scarce.[6] Pino, *et al.*,[5] described the resolution of racemic 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.

(4) Details will be published in a full paper; we wish to thank Mr. Th. G. Aerts for experimental assistance and Mr. F. X. R. van Leeuwen for recording the ORD spectrum.

(5) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962).

(6) (a) R. C. Schulz and E. Kaiser, *Advan. Polym. Sci.*, **4**, 236 (1965); (b) T. Tsuruta, *J. Polym. Sci., Part D*, **6**, 179 (1972).

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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,[1] 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[2] of **1** (3.4×10^{-2} *M*) in ethyl ether–*tert*-butyl 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 spectrum of the photoproduct (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.[4,5] Irradiation of **1** in other solvents also afforded **2** in various yields.[6]

(1) K. Takagi and Y. Ogata, The annual meeting of the Chemical Society of Japan, April 1974, Osaka, Japan, Abstract III, 1611.

(2) 2-Pyridylacetonitrile (**1**) was prepared by dehydration of 2-pyridylacetamide[3]; nmr (CCl_4) δ 8.42 (m, 1 H), 7.43 (m, 3 H), 3.84 (s, 2 H); λ_{max}^{MeOH} 266 nm (ε 1900), 260 (ε 2600), 255 (ε 2300). Preparative-scale photolyses were carried out under nitrogen at 20–25° for 15 hr using an internal water-cooled mercury arc lamp (Halos HIP 300-W).

(3) N. Sperber, D. Papa, E. Schwenk, M. Sherlock, and R. Fricano, *J. Amer. Chem. Soc.*, **73**, 5752 (1951).

(4) J. Pinnow and C. Sämann, *Ber.*, **29**, 624 (1896).

(5) **2**: λ_{max}^{MeOH} 247 nm (ε 6600), 324 (ε 3800); ir (KBr) (cm^{-1}) 3450, 3350, 2200, 1620, 745; nmr (CCl_4) δ 7.3–7.4 (m, 4 H), 4.5 (s, 2 H, exchangeable with D_2O).

(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 Chamelite CS, 2 m at 100–250°). In some cases, an appreciable amount of polymeric material was obtained. In alcohols bearing an α-hydrogen, *e.g.*, ethanol, another photoproduct was obtained which is probably a 1:1 adduct of **1** with the alcohol.[1,7]

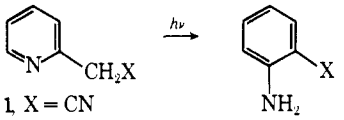
(7) T. J. van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, **94**, 8451 (1972), and references therein.

Table I. Solvent Dependence of Product Formation for the Isomerization of 2-Pyridylacetonitrile (1)[a]

Solvent	% conversion of 1	% formation of 2
Ethyl ether	55.3	8.3
Ethyl ether–*t*-BuOH (1:1 v/v)	38.0	36.8
Acetonitrile	42.7	3.0
Benzene	10.9	22.9
Methanol	65.2	5.2

[a] Pyridylacetonitrile concentrations were 3–7 × 10^{-4} *M*. Irradiation conditions are described in ref 2.

Moreover, irradiation[8] of methyl 2-pyridylacetate (**3**) (1.7 × 10^{-2} *M*) in ethyl ether–*tert*-butyl alcohol gave a product which was identified as methyl *o*-aminobenzoate (**4**) (31%).[9]



1, X = CN
3, X = CO_2CH_3
2, X = CN
4, X = CO_2CH_3

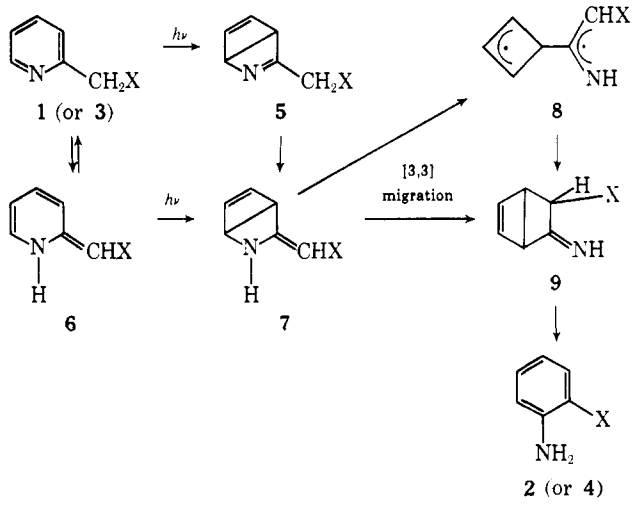
A plot of changes in the absorption spectrum of **1** on irradiation shows the gradual disappearance of **1** with simultaneous increase in absorbance at 248 and 324 nm. The final product, **2** (λ_{max} 248 and 324 nm), is photochemically stable under these conditions. Further, the absence of isosbestic points and the increase of another absorption maximum at *ca.* 280 nm implies the possibility of another pathway to other products.[10]

Unsubstituted α-picoline is known to undergo photolytic valence isomerization to γ-picoline in a poor yield *via* the prismane[13] but not to aniline; hence an electron-attracting group X in the side chain may be necessary for this photoisomerization.

A tentative mechanism for the formation of **2** from **1** is presented in Scheme I. Initial photochemical isomerization of the pyridine ring to a 2,5-bonded Dewar isomer (*e.g.*, **5**) is well known.[11,14] An alternative tautomeric isomer of **5** (*e.g.*, **7**) may be expected from valence isomerization of the methide **6**.

The photolysis of **1** (or **3**) (or their methides, **6**[15]) may initially proceed to the 3-substituted 2-azabicyclo[2.2.0]hexa-2,5-diene (**5**) (or **7**), which is then converted

Scheme I



to a biradical intermediate (**8**) followed by ring closure and then rearomatization to **2** (or **4**).

Alternatively, Dewar pyridine methide (**7**) is in a concerted manner subject to a thermally allowed [3,3] sigmatropic migration to **9** followed by rearomatization to **2** (or **4**).[16]

Precursor **7** to the 3-substituted 2-iminobicyclo[2.2.0]hex-5-ene (**9**) may be formed directly from **6**, since *N*-methyl-2-pyridone, similar to the methide **6**, affords photo-*N*-methyl-2-pyridone (Dewar type) which can be isolated in 20% yield.[17]

Finally, quantum yields for the rearrangement of **1** to **2** vary from 0.02 in acetonitrile to 0.08 in *tert*-butyl alcohol.[18] The rearrangement could not be quenched by piperylene nor could it be caused to occur by a triplet sensitizer such as acetophenone or propiophenone. This suggests that the rearrangement involves a singlet excited state.

(8) Irradiation conditions are the same with ref 2 except for an irradiation time of 12 hr. *Ca.* 360 mg of the starting material was recovered. Methyl 2-pyridylacetate (**3**): λ_{max}^{MeOH} 267 nm (ε 2250), 261 (ε 3000), 255 (ε 2320); nmr (CCl_4) δ 8.34 (m, 1 H), 7.25 (m, 3 H), 3.67 (s, 2 H), 3.59 (s, 3 H).

(9) **4** (a colorless liquid): mass spectrum (*m/e*), 151 (M^+); λ_{max}^{MeOH} 248 nm (ε 6640), 337 (ε 4600); ir (cm^{-1}) (liquid film) 3460, 3360, 2930, 1690, 1620, 750; nmr (CCl_4) δ 7.65 (m, 1 H), 7.1 (m, 1 H), 6.5 (m, 2 H), 4.67 (s, 2 H, exchangeable with D_2O), 3.75 (s, 3 H).

(10) The possibility of accumulation of Dewar-type pyridine (**5**) is less plausible in the respect that Dewar pyridine shows the end absorption at 220 nm alone.[11] The promotion of **1** to the methide form (**6**)[12] by uv light may occur, but this remains to be confirmed.

(11) K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, **92**, 2178 (1970).

(12) S.-O. Chua, M. J. Cook, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 2*, 2111 (1973).

(13) S. Caplain and A. Lablache-Combier, *Chem. Commun.*, 1247 (1970).

(14) (a) K. L. Wierzchowski, D. Shugar, and A. R. Katritsky, *J. Amer. Chem. Soc.*, **85**, 827 (1963). (b) M. G. Barlow, J. G. Dingwall and R. N. Haszeldine, *Chem. Commun.*, 1580 (1970).

(15) While the equilibrium constant for reaction between **1** (or **3**) and **6** is unavailable, the proton exchanges of side-chain methylene with D_2O (excess) proceed in yields of **34** and 55% for **1** and **3**, respectively, at ambient temperature for 1 day. For X = H and Ph, logarithms of the constant, log *K*, are estimated to be 13.28 and 11.88, respectively.[12]

(16) The photoinduced cleavage between the C and N bond of **6** followed by the recyclization to substituted cyclohexadiene, a precursor of **2** (or **4**), may be also envisaged, but the pathway seems to be less feasible on the basis of the necessity of the high energy of the bond (sp^2) compared to the bond (sp^3) of **7**.

(17) (a) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, 86, 950 (1964); (b) R. C. DeSelms and W. R. Schleigh, *Tetrahedron Lett.*, 3563 (1972); (c) H. Furrer, *Chem. Ber.*, 105, 2780 (1972).

(18) The values have the same order as the quantum efficiency of photovalence isomerization of pyridine to Dewar pyridine (quantum yield 0.05).[11]

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Solution Conformation of Acetylcholine and Choline

Sir:

Acetylcholine (ACh) and a large number of its biologically active analogs are known to be important in the transmission of nerve impulses.[1-3] Since the action of biologically active small molecules may depend on conformational changes upon attachment to macromolecular receptors, information about the rotational

(1) D. Nachmanson, *Handb. Sens. Physiol.*, **1**, 18 (1971), and references cited therein.

(2) R. B. Barlow, "Introduction to Chemical Pharmacology," 3rd ed, Methuen, London, 1964.

(3) M. Martin-Smith, G. Smail, and J. B. Stenlak, *J. Pharm. Pharmacol.*, **19**, 561 (1967).