spectra were recorded on a Perkin-Elmer 137 instrument. Analytical gas chromatography was carried out on a Varian 2700 all-glass chromatograph equipped with flame ionization detectors, using a 6 ft × 0.25 in. o.d. glass column with 3% SE-30 on Chromosorb Q at 175 °C. All solvents were Aldrich spectrophotometric grade and were used without further purification.

***trans*-4,4-Dimethyl-2,3,5-trioxabicyclo[4.4.0]decane (1).** Peroxide 1 was prepared by the procedure of Payne and Smith.[8] Purification was accomplished by distillation [bp 45–50 °C (0.5 mm)], followed by repeated recrystallization from pentane to yield 15% of the analytically pure peroxide: mp 24–25 °C; IR ($CCl_4$) 3.3, 7.3–7.4 (*gem*-dimethyls), 8.2, 9.3, 10.6 μm; NMR ($CCl_4$) δ 1.3 (s, 3 H), 1.6 (s, 3 H), 3.68 (m, $J$ = 11, 8, 3.5 Hz).

**Procedure for Determination of Reaction Rate.** Solutions of peroxide 1, typically $2.5 \times 10^{-2}$ M, and an internal standard, usually decane, were prepared in Pyrex test tubes. The samples were degassed at $5 \times 10^{-4}$ mm through three freeze–pump–thaw cycles and sealed under vacuum. The tubes were then thermolyzed and analyzed at intervals by gas chromatography as described. The rate of reaction of the peroxide and appearance of acetone were both first order. The rate constants were extracted from these data by least-squares analysis and are reported in the Table I.

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**Registry No.**—1, 64235-36-5; 2, 67-64-1; 3, 1072-21-5.

## References and Notes

(1) W. Adam and N. Duran, *J. Am. Chem. Soc.*, **99**, 2729 (1977).
(2) W. Adam and J. Sanabia, *Angew. Chem., Int. Ed. Engl.*, **12**, 843 (1973).
(3) T. Goto and H. Nakamura, *Tetrahedron Lett.*, 4627 (1976).
(4) M. Schultz, unpublished data quoted in "Organic Peroxides", Vol. 3, D. Swern, Ed., Wiley, New York, N.Y., 1972, p 116; R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **96**, 2955 (1974); W. Adam and A. Rios, *Chem. Commun.*, 822 (1971).
(5) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Papplaonnou, *J. Am. Chem. Soc.*, **92**, 4927 (1970).
(6) J. Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 5403 (1977).
(7) S. W. Benson, F. R. Cruickshank, D. B. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(8) G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1682 (1957).

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## β Radioloysis of Crystalline $^{14}C$-Labeled Amino Acids

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In an investigation of the possible validity of the Vester–Ulbricht β-decay parity violation mechanism[1–3] for the abiotic origin of molecular chirality, one of us has recently shown[4,5] that 10–20% net longitudinally polarized 120-keV electrons produced in a linear accelerator caused the asymmetric degradation of DL-leucine. "Natural" antiparallel spin-polarized electrons preferentially degraded the D-leucine component of the racemate, and parallel spin electrons selectively destroyed the L enantiomer. This was the first positive demonstration of asymmetric degradation by β particles since Garay's 1968 report[6] that 0.36 mCi of $^{90}SrCl_2$ in aqueous solution caused more rapid decomposition of dissolved D-tyrosine than of L-tyrosine. Earlier studies[1–3,7] and our subsequent attempts[8,9] to modify and extend Garay's experiments to other amino acids, both solid and dissolved, using a 61 700-Ci $^{90}Sr$–$^{90}Y$ source at Oak Ridge National Laboratory led to no observable asymmetric radiolyses. More recently, Darge and co-workers[10] made the remarkable report that DL-tryptophan in frozen aqueous solution suffered 33% total degradation and (based on its optical rotation of 0.0007 ± 0.0004°) a 19% optical enrichment of the D enantiomer during its 12-week exposure to 0.63 mCi of dissolved [$^{32}P$]phosphate. In view of the several positive reports of asymmetric β radiolysis reviewed above, we have been encouraged to examine for β-induced optical activity a number of $^{14}C$-labeled DL amino acids of high specific radioactivity (~300–600mCi/mol) prepared 17–25 years ago at the Lawrence Berkeley Laboratory, University of California.

The racemic amino acids studied and the radiochemical and analytical data pertaining to them are recorded in Table I. Three of the amino acids listed in Table I (DL-Ala, DL-Asp, and DL-Nva) have been examined previously[11] for optical activity (using ORD measurements) and percent decomposition (using the amino acid analyzer), with the observation of no selective radiolysis. In the present study we have used quantitative gas chromatography (GC) as our analytical criterion for both the enantiomeric composition of the undecomposed amino acid residues as well as for percent degradation (using the "enantiomeric marker" technique[12]). GC not only provides the important advantage (over optical rotation) of looking at *only* the residual enantiomers of interest (uncontaminated by accompanying degradation products which may or may not be optically active) but is capable, particularly with microquantities, of superior accuracy and precision (~0.2%)[13] in the quantitative analysis of enantiomers. The DL amino acids in Table I were converted to their *N*-trifluoroacetyl isopropyl esters as previously described[13] and analyzed in replicate with the aid of a digital electronic integrator,[13] using 150 ft × 0.02 in stainless steel capillary GC columns[13] coated with the optically active GC phases *N*-lauroyl-L-valine *tert*-butylamide.[14] or *N*-docosanoyl-L-valine *tert*-butylamide.[15] All GC analyses were interspersed "back-to-back" with an equal number of replicate GC analyses of the corresponding nonradioactive, authentic DL amino acid as a control. For comparison purposes, Table I also summarizes radiochemical, percent decomposition, and enantiomeric composition data, similarly obtained, for a number of labeled D and L amino acids, which had been prepared by optical resolution of several of the racemic amino acids in Table I.

The enantiomeric compositions in Table I indicate that the D/L ratios of the radioactive DL amino acids examined are 50:50, within experimental error, and that they suffered no asymmetric degradation, despite self-radiolyses as high as 67%. The enantiomeric compositions of the resolved amino acids show further that racemization does not necessarily accompany self-radiolysis in the dry state, although comparison of the enantiomeric compositions noted for D-norvaline-*3*-$^{14}C$ and D-leucine-*3*-$^{14}C$ with those estimated from the original optical rotations of the samples suggests that some racemization may be possible. From the specific radioactivity of the samples and their ages, one can calculate the number of β particles emitted during the lifetimes of the samples. From these numbers (not shown) and the percent decompositions, one can calculate the number of molecules decomposed per β particle, which proves to vary between about 6000 and 36 000 among our samples. These numbers are higher than the ~3000 molecules decomposed per electron observed during our previously reported[4] asymmetric degradations of DL-leucine with longitudinally polarized linear accelerator electrons. The variability in the percent decomposition and hence the number of molecules decomposed per electron, as well as the *G* values observed for comparable samples (e.g., D-, L-, and DL-valine-*4,4'*-$^{14}C$, D- vs. DL-leucine-*3*-$^{14}C$, etc.), is noteworthy and may be due, we suspect, to the variability of trace impurities, including moisture, in the 17–25-year-old samples. Finally, the racemic nature of the radiolyzed DL amino acids in Table I further indicates that microbial degradation could not have been operative during the lifetimes

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Table I

| Amino acid | Registry no. | Radioactivity, mCi/mol | Age,[a] years | Total dose, rads $\times 10^{-7}$ | Percent decomposed | Molecules decomposed per electron $\times 10^{-4}$ | $G$[b] | Enantiomeric composition %D | %L | SD[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| DL-Alanine-2-$^{14}C$ | 4548-47-4 | 285 | 16.9 | 5.05 | 26.5 | 2.84 | 56.8 | 50.06[c] | 49.94 | ±0.85 |
| DL-Valine-4,4′-$^{14}C$ | 5776-57-8 | 316 | 25.8 | 6.51 | 30.0 | 1.90 | 38.0 | 50.19[c] | 49.81 | ±0.20 |
| DL-Norvaline-3-$^{14}C$ | 3409-47-0 | 574 | 24.9 | 11.41 | 17.4 | 0.63 | 12.6 | 49.94[c] | 50.06 | ±0.18 |
| DL-Leucine-3-$^{14}C$ | 3409-50-5 | 446 | 24.0 | 7.63 | 67.8 | 3.26 | 65.2 | 50.15[c] | 49.85 | ±0.22 |
| DL-Norleucine-3-$^{14}C$ | 64235-74-1 | 551 | 24.9 | 9.78 | 24.1 | 0.90 | 18.0 | 50.10[c] | 49.90 | ±0.17 |
| DL-Aspartic-4-$^{14}C$ acid | 19701-77-0 | 319 | 24.1 | 5.40 | ~50 | 3.35 | 67.0 | 50.23[c] | 49.77 | ±1.02 |
| D-Valine-4,4′-$^{14}C$ | 64235-81-0 | 316 | 21.3 | 5.37 | 31.2 | 2.39 | 47.8 | 100.00 | 0.00 | |
| L-Valine-4,4′-$^{14}C$ | 64235-72-9 | 316 | 21.3 | 5.37 | 47.1 | 3.62 | 72.4 | 0.00 | 100.00 | |
| D-Norvaline-3-$^{14}C$ | 64235-71-8 | 574 | 20.5 | 9.39 | 21.1 | 0.92 | 18.4 | 93.95 | 6.05 | ±0.21 |
| L-Norvaline-3-$^{14}C$ | 64235-70-7 | 574 | 20.5 | 9.39 | 20.3 | 0.89 | 17.8 | 0.87 | 99.13 | |
| D-Leucine-3-$^{14}C$ | 64235-69-4 | 446 | 20.6 | 6.55 | 39.5 | 2.22 | 44.4 | 92.55 | 7.45 | ±0.11 |
| D-Norleucine-3-$^{14}C$ | 64235-68-3 | 551 | 20.6 | 8.09 | 25.9 | 1.17 | 23.4 | 99.80 | 0.20 | |
| L-Norleucine-3-$^{14}C$ | 64235-67-2 | 551 | 20.6 | 8.09 | 18.6 | 0.84 | 16.8 | 0.80 | 99.20 | |

[a] Between date of preparation and date of analysis. [b] Molecules decomposed per 100 eV, assuming average energy per $\beta = 5.0 \times 10^4$ eV. [c] Corrected to a D/L ratio of 50:50 for composition of authentic DL standard. [d] SD denotes standard deviation for 3–5 replicate GC analyses.

of the samples, since if it had an excess of D enantiomer it should be observed in the residual materials.

Even though $^{14}C$ $\beta$ particles are relatively low energy (endpoint energy 155 keV,[16] mean energy ~50 keV), their polarization is substantial. Both theoretically and experimentally,[17] $\beta^{\pm}$ particles emitted with velocity $v$ during weak nuclear decays have a helicity (longitudinal polarization along their direction of motion) of $\mp v/c$. This is a direct consequence of the two-component neutrino theory which predicted the nonconservation of parity.[18] Since the kinetic energy of the electron is related to its rest energy $mc^2$ by eq 1,[19] it follows that $v/c$ is given by eq 2. Since the rest energy $mc^2$ of the electron is 511 keV,[20] this implies a polarization for $^{14}C$ betas of 64.1% at the endpoint energy and 41.3% at the middle (50 keV) of the energy spectrum. Subsequent ionization processes which slow down the primary electron decrease its energy on the average only by ~30 eV per ion pair produced,[21] and furthermore it is known[22] that such ionizations leave the longitudinal polarization of the primary electron virtually unchanged until it has been slowed down to a few keV.[23] We thus conclude that the polarization of the primary electrons available for initiating chiral destruction of the substrate in the $^{14}C$ experiments is somewhat greater than the polarization (10–20%) of the electrons employed in the accelerator experiments.[4,5]

$$T = mc^2[(1 - v^2/c^2)^{1/2} - 1] \quad (1)$$

$$v/c = (2T/mc^2)^{1/2}(1 + T/2mc^2)^{1/2}/(1 + T/mc^2) \quad (2)$$

Thus, the failure to observe asymmetric $\beta$ radiolysis in the solid DL amino acid samples listed in Table I, as compared to the small but successful asymmetric degradations previously induced[4,5] in DL-leucine by the 10–20% net longitudinally polarized linear accelerator electrons, is at first appearance puzzling. We believe, however, that the discrepancy may be rationalized as follows. As is apparent (Table I) from the large number of molecules decomposed for each $^{14}C$ beta emitted, the majority of the degradations must be engendered by secondary electrons produced by numerous subsequent ionizations caused by the primary $^{14}C$ $\beta$ particles. The degree of polarization, if any, of such secondary electrons is not known[3] but presumably it is at best considerably less than that of the primary $\beta$ particles, and furthermore the energies of the secondary electrons (~30-eV average[21]) are in a range more suitable for initiating chemical changes.[24] For these reasons, it seems possible that the differing sample geometries in the two types of experiments might be crucial. In the accelerator experiments the amino acid target was a thin layer in a plane perpendicular to the impinging 120-keV electron beam, while the $^{14}C$ amino acids were thick bulk samples isotropically irradiated by internally produced $\beta$ particles. The latter geometry clearly allows for the preferential production and intervention of less polarized (or unpolarized) secondary electrons, which in turn cause greater degradation of a less asymmetric (or totally symmetric) nature. This possibility is emphasized by the fact that up to 36 000 molecules were decomposed per primary $\beta$ particle in the $^{14}C$-labeled samples (Table I), whereas only ~3000 molecules per (higher energy) electron were destroyed in the accelerator experiments.[4,5] Another difference of possible significance is the differing time scale involved in the two types of experiment. The accelerator samples were irradiated for a matter of hours only and were analyzed immediately thereafter, whereas the $^{14}C$-labeled samples suffered self-radiolysis during several decades prior to their GC analyses. Clearly the possibility of migration within the crystal lattice of the initial degradation fragments and possible secondary decompositions subsequently engendered by them is much greater in the $^{14}C$ samples. Such presumably symmetrical processes could conceivably reduce the net asymmetric effect to undetectable levels. It should be mentioned finally that circularly polarized bremsstrahlung produced by the initial longitudinally polarized $\beta$ particles, which had been originally postulated[1-3] as the source of asymmetric *photochemical* effects which might produce optical activity, has recently been shown[25,26] on energetic grounds to be ineffective in engendering even significant gross degradation of the target sample. Other problems regarding the $\beta$-decay mechanism for the origin of optical activity involving $^{14}C$ and $^{40}K$ $\beta$ particles have recently been discussed by us.[27]

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## References and Notes

(1) F. Vester, T. L. V. Ulbricht, and H. Krauch, *Naturwissenschaften*, **46**, 68 (1959).
(2) T. L. V. Ulbricht, *Q. Rev., Chem. Soc.*, **13**, 48 (1959).
(3) T. L. V. Ulbricht and F. Vester, *Tetrahedron*, **18**, 629 (1962).
(4) W. A. Bonner, M. A. Van Dort, and M. R. Yearian, *Nature (London)*, **258**, 419 (1975); **264**, 198 (1976).
(5) W. A. Bonner, M. A. Van Dort, M. R. Yearian, H. D. Zeman, and G. C. Li,

*Israel J. Chem.*, **15**, 89 (1976/77).
(6) A. S. Garay, *Nature (London)*, **219**, 338 (1968).
(7) V. I. Goldanskii and V. V. Khrapov, *Sov. Phys. JETP (Engl. Transl.)*, **16**, 582 (1963).
(8) W. A. Bonner, *J. Mol. Evol.*, **4**, 23 (1974).
(9) W. A. Bonner and J. J. Flores, *Origins Life*, **6**, 187 (1975).
(10) W. Darge, I. Laczko, and W. Thiemann, *Nature (London)*, **261**, 522 (1976).
(11) W. J. Bernstein, R. M. Lemmon, and M. Calvin in "Molecular Evolution, Prebiological and Biological", D. L. Rolfing and A. Oparin, Ed., Plenum, New York, N.Y., 1972, pp 151–155.
(12) W. A. Bonner, *J. Chromatogr. Sci.*, **11**, 101 (1973).
(13) W. A. Bonner, M. A. Van Dort, and J. J. Flores, *Anal. Chem.*, **46**, 2104 (1974).
(14) B. Feibush, *Chem. Commun.*, 544 (1971).
(15) R. Charles, U. Beitler, B. Feibush, and E. Gil-Av, *J. Chromatogr.*, **112**, 121 (1975).
(16) D. E. Gray, Ed., "American Institute of Physics Handbook", McGraw-Hill, New York, N.Y., 1957, pp 8–98.
(17) H. Frauenfelder, and R. Steffen in "$\alpha$, $\beta$, and $\gamma$-Ray Spectroscopy", Vol. 2, K. Siegbahn, Ed., North-Holland Publishing Co., Amsterdam, 1965, pp 1431–1452.
(18) T. D. Lee and C. N. Yang, *Phys. Rev.*, **104**, 254 (1956).
(19) P. G. Bergmann, "Introduction to the Theory of Relativity", Prentice-Hall, New York, N.Y., 1942, p 92, eq 6.20.
(20) N. Barash-Schmidt et al., *Rev. Mod. Phys.*, **48**, 5 (1976).
(21) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry", New York, N.Y., 1964, p 70ff.
(22) J. Heintze, *Z. Phys.*, **150**, 134 (1958).
(23) J. D. Jackson, private communication to H.P.N.
(24) C. E. Klots in "Fundamental Processes in Radiation Chemistry", P. J. Ausloos, Ed., Interscience, NewYork, N.Y., 1968, p 36.
(25) L. Keszthelyi, *Nature (London)*, **264**, 197 (1976).
(26) D. C. Walker, *Origins Life*, **7**, 383 (1976).
(27) H. P. Noyes, W. A. Bonner, and J. A. Tomlin, *Origins Life*, **8**, 21 (1977).

## Abnormal Products in the Siegrist Reaction Involving Ortho-Fluorinated Intermediates[1]

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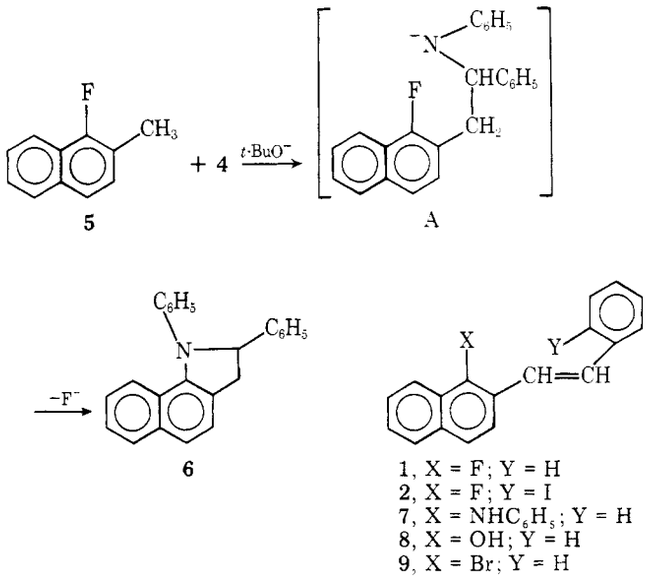
The syntheses of *trans*-1-(1 fluoro-2-naphthyl)-2-phenylethylene (**1**) and *trans*-1-(1-fluoro-2-naphthyl)-2-(*o*-iodophenyl)ethylene (**2**) via the Wittig reaction as intermediates for the attempted photochemical synthesis of 7-fluorobenz[*a*]anthracene (**3**) have been described.[3] Unfortunately, insufficient **3** was made (only via **2** as use of **1** failed) for adequate testing for possible carcinogenic activity. Because of our interest in preparing larger amounts of **3**, we wished to develop improved methods for the synthesis of **1** and **2**.

A route to substituted stilbenes which involves condensation of methylated aromatic nuclei with benzalaniline (**4**) in the presence of potassium *tert*-butoxide (eq 1) has been studied[4] and applied to the facile synthesis of hexahelicene and other helicenes.[5] However, no example involving an ortho halogen-substituted reactant has been reported.

$$\mathrm{ArCH_3} + \underset{\mathbf{4}}{\mathrm{C_6H_5N{=}CHC_6H_5}} \rightarrow \mathrm{ArCH{=}CHC_6H_5} + \mathrm{C_6H_5NH_2} \quad (1)$$

Consequently, we attempted to react 1-fluoro-2-methylnaphthalene (**5**) and **4** as above. None of the expected **1** was obtained. Instead, a complex mixture was produced from which small amounts of 2,3-dihydro-1,2-diphenylindole (**6**), *trans*-(1-anilino-2-naphthyl)-2-naphthyl)-2-phenylethylene (**7**), and *trans*-1-(1-hydroxy-2-naphthyl)-2-phenylethylene (**8**) were isolated. A similar reaction with 1-bromo-2-methylnaphthalene and **4** afforded *trans*-1-(1-bromo-2-naphthyl)-2-phenylethylene (**9**) in 58% yield with no evidence for the formation of nitrogenous products.

Scheme I




The formation of **6** probably occurs by intramolecular nucleophilic displacement of fluoride ion by anion A, produced by the addition of the 1-fluoro-2-naphthylmethyl anion to **4**, as shown in Scheme I. The formation of **7** evidently involves a base-catalyzed cleavage of a C–N bond in **6** to form **7**. We have shown that under the reaction conditions **6** is converted to **7**. The formation of **8** probably occurs by displacement of the fluorine in **5** by *tert*-butoxide followed by a normal Siegrist reaction and pyrolytic cleavage of the resulting *tert*-butyl ether.

Interestingly, the elimination of aniline to form **9** occurs more rapidly than intramolecular displacement of bromide ion in the bromo intermediate corresponding to A. Evidently, the bromine in **9** is relatively much more stable to attack by *tert*-butoxide ion or to intramolecular attack by a nitrogenous anion similar to A than is the fluorine in **1** (or A). To our knowledge the contrasting results in the reactions of **4** with 1-fluoro-2-methylnaphthalene (**5**) and with 1-bromo-2-methylnaphthalene provide the first evidence that the intramolecular nucelophilic displacement of fluoride occurs more easily than that of bromide. Some, but not all, evidence shows that aryl fluorides are more reactive than aryl bromides in intermolecular nucleophilic substitution.[6] The same conclusion was reached in a study[7] on the action of potassium *tert*-butoxide in $Me_2SO$ on chloro-, bromo- and iodonaphthalenes which showed that the reactions proceeded via 1,2-naphthyne to give mixtures of 1- and 2-*tert*-butoxynaphthalenes, whereas both 1- and 2-fluoronaphthalene formed 1- and 2-*tert*-butoxynaphthalenes, respectively, by direct displacement of fluoride.

In order to obtain evidence as to the mechanism of formation of **6** and **7** in the Siegrist reaction, we prepared **1** as described[3] from **5**,[8] prepared in improved yield (63%) by using the diazonium hexafluorophosphate[9] instead of the diazonium tetrafluoroborate.[8] On heating **1** with aniline under conditions identical to those involved in the reaction of **4** and **5**, there was obtained neither **6** nor **7**, and 85% of **1** was recovered. This fact supports the intramolecular mechanism for the formation of **6** shown in Scheme I.

When *o*-fluorotoluene was treated with **4** a 28% yield of 1-(*o*-fluorophenyl)-2-phenylethylene (**10**) was obtained, but no attempt to maximize the yield nor to isolate other components was made. Thus, the fluorine in **10** is less reactive than the fluorine in **1** under Siegrist conditions.

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