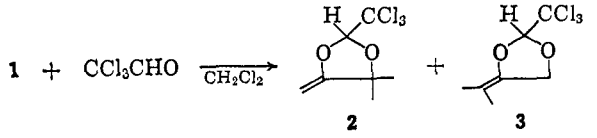
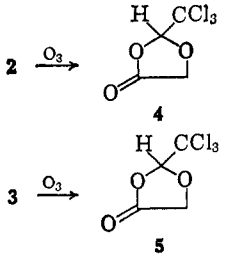
Addition of trichloroacetaldehyde (50% excess) to a methylene chloride solution (reflux) of 2,2-dimethylcyclopropanone (**1**) followed by refluxing yields the cyclic enol ethers **2** (16%) (nmr[7] ($CCl_4$) δ 1.46 (3 H, s), 1.57 (3 H, s), 3.90 (1 H, d, $J$ = 3 Hz), 4.40 (1 H, d, $J$ = 3 Hz), 5.53 (1 H, s); ir $\lambda_{max}^{CCl_4}$ 5.90 μ (C=C); mass spectra at 75 eV, *m/e* (relative intensity) 234 (1.1), 232 (3.6), 230 ($M^+$, 3.7) 121 (1.8), 119 (5.0), 117 (5.1), 113 (84), 84 (82), 67 (100), 56 (89), 49 (99), 41 (80)) and **3** (1.5%) (nmr ($CCl_4$) δ 1.57 (3 H, s), 1.74 (3 H, m), 4.43–4.97 (2 H, m) 5.54 (1 H, s); ir $\lambda_{max}^{CCl_4}$ 5.78 μ (C=C); mass spectra (75 eV) 234 (3.1), 232 (9.7), 230 ($M^+$, 10.3), 113 (33)).




**2** **3**

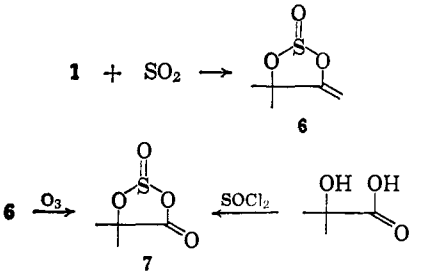
Spectral evidence indicates that PhCHO and $CH_3CHO$ form adducts similar to **2**. Compounds **2** and **3** were further characterized by ozonolysis to the lactones **4** (nmr ($CH_2Cl_2$) δ 1.51 (3 H, s), 1.58 (3 H, s), 5.78 (1 H, s); ir $\lambda_{max}^{CH_2Cl_2}$ 5.50 μ (C=O); mass spectra (75 eV) 121 (0.89), 119 (2.8), 117 (3), 115 (24), 87 (45), 59 (100)) and



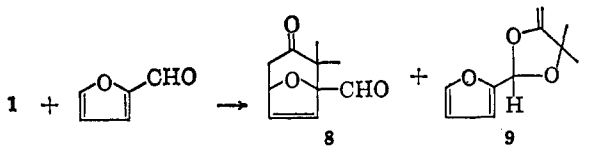

**5** (nmr ($CCl_4$) δ 4.48 (2 H, AB, $J_{AB}$ = 14 Hz, $\Delta V_{AB}$ = 10 Hz, second order splitting), 5.85 (1 H, second-order splitting); ir $\lambda_{max}^{CCl_4}$ 5.44 μ (C=O)).

Addition of $SO_2$ to methylene chloride solutions of **1** yields the adduct **6** (nmr (neat) δ 1.49 (3 H, s), 1.87 (3 H, s), 4.33 (1 H, d, $J$ = 3.0 Hz), 4.66 (1 H, d, $J$ = 3.0 Hz); ir $\lambda_{max}^{neat}$ 3.22 μ (C=CH), 5.99 μ (OC=C); mass spectra, *m/e* 148 ($M^+$), 84 (24), 69 (20), 56 (68), 48 (20)).

The structure of **6** was proven by ozonolysis to the ketone **7** which was compared with authentic material.[8]

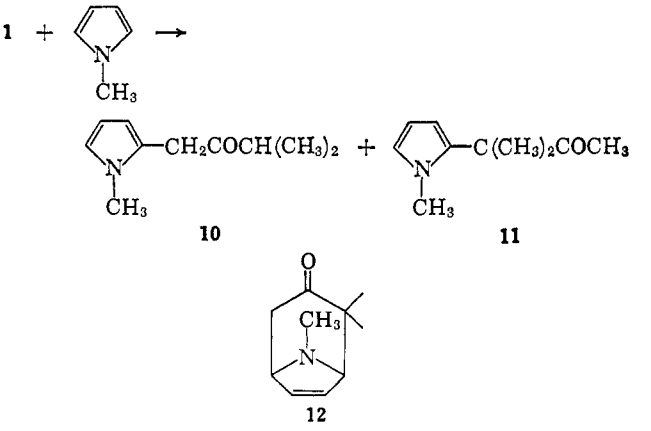



Furfural and **1** yield the cycloadducts **8** (nmr ($CCl_4$) δ 1.11 (3 H, s), 1.23 (3 H, s), 2.59 (2 H, AB, $J_{AB}$ = 16 Hz, $\Delta V_{AB}$ = 39.2 Hz, low-field half split $J$ = 5 Hz, high-field half split $J$ = 1.5 Hz), 5.13 (1 H, d of t, $J$ = 5 Hz, 1.5 Hz), 6.36 (2 H, AB, $J_{AB}$ = 6 Hz, $\Delta V_{AB}$ = 7.75 Hz, low-field half split $J$ = 1.5 Hz), 9.77 (1 H, s); ir $\lambda_{max}^{CCl_4}$ 5.88 μ, 5.93 μ; mass spectra (75 eV), *m/e* 180 ($M^+$)) and **9** (nmr ($CCl_4$) δ 1.42 (3 H, s), 1.48 (3 H, s), 3.82 (1 H, d, $J$ = 2.5 Hz), 4.24 (1 H, d, $J$ = 2.5 Hz), 6.13 (1 H, s), 6.28–6.53 (2 H, m), 7.43 (1 H, m); mass spectra (75 eV), *m/e* 180 ($M^+$)).




**8** **9**

Addition of N-methylpyrrole to **1** results in formation[9] of the substitution adducts **10** (nmr ($CCl_4$) δ 0.97 (1 H, d, $J$ = 7 Hz), 2.7 (1 H, septet, $J$ = 7 Hz), 3.4 (3 H, s), 3.56 (2 H, s), 5.88 (2 H, m), 6.43 (1 H, t, $J$ = 2 Hz); ir $\lambda_{max}^{CCl_4}$ 5.85 μ; mass spectra (75 eV), *m/e* 165 ($M^+$)) and **11** (nmr ($CCl_4$) 1.43 (6 H, s), 1.87 (~3 H, s), 5.89 (~2 H, m), 6.45 (~1 H, t) $J$ = 2 Hz); ir $\lambda_{max}^{CCl_4}$ 5.86 μ; mass spectra (75 eV), *m/e* 165 ($M^+$)) as the major 1:1 products (ratio of **10**:**11** was 5:1).




**10** **11** **12**

The mechanisms of these reactions are presently under investigation.

(7) TMS internal standard. Satisfactory mass spectral or elemental analyses were obtained for all new compounds reported.

(8) E. Blaise and A. Montagne, *Compt. Rend.*, **174**, 1553 (1922).

(9) A mixture of $CH_2Cl_2$ and excess N-methylpyrrole was cooled to −78°. A $CH_2Cl_2$ solution of **1** was added and the resulting mixture was left standing at −78° for several days. The solvent was then stripped off at room temperature and the residue was worked up by preparative vpc. At this time it is uncertain whether **10** and **11** are primary products or are products of the rearrangement of **12**.

(10) Alfred P. Sloan Fellow.

(11) National Science Foundation Predoctoral Fellow, 1966–present. National Science Foundation Predoctoral Trainee, 1965–1966.

(12) National Institutes of Health Postdoctoral Fellow, 1967–1968.

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## Topography of Nucleic Acid Helices in Solutions. VIII. Selective Interactions of L-Amino Acids and Peptides with Nucleic Acid Helices[1]

*Sir:*

One of the intriguing problems in biochemistry is the universality of the L-amino acids in proteins and D-ribose and D-deoxyribose in nucleic acids. Two basic questions may be asked: (a) "how were these particular isomers selected originally?" and (b) "what is the basic relationship, if any, between the protein helical conformation based on a chain structure composed of

(1) For part VII in this series see E. J. Gabbay and R. R. Shimshak, *Chem. Commun.*, submitted for publication.

Table I. Effect of $2 \times 10^{-2}$ *M* Diamino Acids, II, on the $T_m$ of the Helix–Coil Transition of rI–rC, rA–rU, and Calf Thymus DNA in 0.025 *M* Sodium Phosphate Buffer (0.025 *M* in $Na^+$), pH 6.25, and 0.02 *M* NaCl

| Compd | $T_m$, deg[a-c] rI–rC | rA–rU | Calf thymus DNA | No. of positive[d] charges/molecule at 25.0° | 50.0° | 75.0° |
|---|---|---|---|---|---|---|
| L-Diaminopropionic acid | 63.0 | 51.3 | 78.3 | 1.76 | 1.57 | 1.37 |
| L-Diaminobutyric acid | 64.2 | 51.8 | 81.0 | 2.00 | 2.00 | 1.97 |
| DL-Diaminobutyric acid | 62.2 | 51.4 | 81.0 | 2.00 | 2.00 | 1.97 |
| L-Ornithine | 61.6 | 51.8 | 78.2 | 2.00 | 2.00 | 2.00 |
| DL-Ornithine | 59.4 | 51.8 | 78.0 | 2.00 | 2.00 | 2.00 |
| L-Lysine | 56.6 | 49.5 | 78.6 | 2.00 | 2.00 | 2.00 |
| D-Lysine | 56.1 | 49.4 | 77.9 | 2.00 | 2.00 | 2.00 |

[a] Melting curves were measured in 1-ml cuvettes thermostated with a Haake constant-temperature water circulator equipped with a Neslab temperature programmer. A Gilford Model 240 spectrophotometer equipped with automated recording accessories was used, and the temperature of the cell compartment was measured directly by using an iron–constantan thermocouple connected to a Leeds-Northrup Model 8290 potentiometer. [b] The $T_m$ of the rI–rC (Miles Labs), rA–rU (Calbiochem), and calf thymus DNA (Calbiochem) in the absence of the diamino acids II are found to be 50.3 ± 0.4°, 44.6 ± 0.2°, and 73.4 ± 0.3°. (It should be noted that the previously reported $T_m$ of rI–rC[3] and rA–rU[3] of 48.8 ± 0.4° and 46.4 ± 0.4°, respectively, refer to different lot number and source of material.) [c] $T_m$ curves of the nucleic acid helices in the presence of the salts II were run concurrently for each pair, *i.e.*, L and DL mixtures. Under these conditions $\Delta T_m$ [$T_m$(L) − $T_m$(D or DL)] is found to be reproducible to within ±0.3°. [d] Titration curves of the diamino acids II in 0.025 *M* NaCl were performed using a Radiometer automatic titrator.

L-amino acids and the nucleic acid helical structure based on a chain composed of alternating D-pentose and phosphate residues?"[2] In an attempt to shed light on the second question, Gabbay and Kleinman[3] have shown recently that the L enantiomers of the amino acid amides of the general structure I, $^+NH_3CHRCONHCH_2CH_2NMe_2H^+2Br^-$, interact more strongly with nucleic acid helices than the corresponding D enantiomers. In this paper, we wish to report that the preference for the L enantiomers appears to be general for other amino acids and their derivatives. The effect of diamino acids of the general structure II, $^+NH_3CH(CO_2^-)(CH_2)_nN^+H_3 \cdot Cl^-$, and lysyl dipeptides III, $^+NH_3CH((CH_2)_4N^+H_3)CONHCHRCO_2^- \cdot Br^-$, on the melting temperature of polyriboinosinic–polyribocytidylic acids (rI–rC), polyriboadenylic–polyribouridylic acids (rA–rU), and calf thymus DNA is reported in Tables I[3] and II, respectively.

Several interesting points may be made. (1) There is very little difference in the degree of stabilization of polyriboadenylic–polyribouridylic (rA–rU) and calf thymus DNA helices by the L and DL mixture of the diamino acids II. However, there is a very large difference in the degree of stabilization of the polyriboinosinic–polyribocytidylic helix which is consistent with our earlier studies on this system.[3] (2) The degree of stabilization of the helices by the diamino acids II is considerably lower than the diammonium salts IV, $^+NH_3(CH_2)_nN^+H_3 \cdot 2Br^-$, due to the presence of the negatively charged carboxyl group.[4] (3) The effect of the neighboring negatively charged group is seen dramatically in the lysine system. For example, approximately the same degree of stabilization of the rI–rC and rA–rU helices are obtained by the lysyl dipeptides III at one-tenth the concentration of lysine (Tables I and II). (4) The LL-lysyl dipeptides stabilize the nucleic acid helices to a greater degree than the corresponding DD-lysyl dipeptides. Although the difference in the degree of stabilization of calf thymus DNA by the LL and DD enantiomers is not substantial, it is still outside the experimental error.

(2) H. Erying, L. L. Jones, and J. D. Spikes in "Horizon in Biochemistry," M. Kasha and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1962.

(3) E. J. Gabbay, *Biochemistry*, **5**, 3036 (1966); E. J. Gabbay, *Biopolymers*, **5**, 726 (1967); E. J. Gabbay and R. Kleinman, *J. Am. Chem. Soc.*, **89**, 7123 (1967).

Table II. The Effect of $2 \times 10^{-3}$ *M* Lysyl Dipeptides on the $T_m$ of the Helix–Coil Transition of rI–rC, rA–rU, and Calf Thymus DNA in 0.025 *M* Sodium Phosphate Buffer (0.025 *M* in $Na^+$), pH 6.25[a-d]

| Compd | $T_m$, deg[a-c] rI–rC | rA–rU | Calf thymus DNA | No. of positive[d] charges/molecule at 30.0° | 50.0° |
|---|---|---|---|---|---|
| L-Lysyl-L-leucine | 56.4 | 48.1 | 76.8 | 1.98 | 1.95 |
| D-Lysyl-D-leucine | 54.6 | 46.7 | 76.1 | 1.98 | 1.95 |
| L-Lysyl-L-phenylalanine | 53.2 | 46.3 | 75.2 | 1.91 | 1.84 |
| D-Lysyl-D-phenylalanine | 51.8 | 45.5 | 74.8 | 1.91 | 1.84 |
| L-Lysylglycine | 53.4 | 46.6 | 75.0 | 1.94 | 1.87 |

[a-d] Same as in Table I.

The nature of the difference between the interaction of the L and D enantiomers with nucleic acid helices is not clear. A general phenomenon is being observed, namely, a greater degree of stabilization of nucleic acid helices by the L-amino acid derivatives, *i.e.*, the amide salts I, $^+NH_3CHRCONHCH_2CH_2N^+Me_2H \cdot 2Br^-$, the diamino acids II, $^+NH_3CH(CO_2^-)(CH_2)_n \cdot N^+H_3 \cdot Cl^-$ where $n$ = 2, 3, and 4, and lysyl dipeptides III, $^+NH_3CH((CH_2)_4N^+H_3)CONHCHRCO_2^- \cdot Br^-$. The results are clearly indicative of a selective interaction.[5]

**Acknowledgment.** This work was supported by the Rutgers Research Council and by Grants GM-13597 and GM-15308 from the U. S. Public Health Service. We wish to thank the National Science Foundation for a summer undergraduate fellowship to R. R. S.

(4) In the presence of $2 \times 10^{-2}$ *M* IV in 0.025 *M* sodium phosphate buffer the $T_m$ of the rI–rC is found to be 83.0, 83.6, and 78.0° for $n$ = 2, 3, and 4, respectively.

(5) E. J. Gabbay, manuscript in preparation (1968).

(6) National Science Foundation Predoctoral Trainee, 1965–1968.

(7) Henry Rutgers Fellow.

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## The Radical-Catalyzed Rearrangement of Trisilanethiols[1]

*Sir:*

The transformation of hexamethyldisilane to trimethyl[(dimethylsilyl)methyl]silane, which occurs in the

(1) This work was supported in part by the Electronic Technology Division of the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract No. AF-33(615)-67-C-1175.