that of a right-handed helix.[11] However, the interpretive basis for this type of calculation is that the protein consists of two kinds of conformational regions, one having the rotatory properties of a right-handed α-helix, the other having those of a random polypeptide. If this interpretation is correct, the same linear combination of rotations (13% helix, 87% random coil) should account for the dispersion at wave lengths other than 233 mμ. This is not the case with RNase. In particular the low helical content predicted from the amplitude of the Cotton effect at 233 mμ cannot account for the swing to positive rotations at lower wave lengths. It is our interpretation that the negative Cotton effect provides evidence for the presence of right-handed α-helices in RNase but that the simple two-state model does not lead to a consistent explanation of the observed dispersion, so that a meaningful helix content cannot be calculated. Experiments at lower wave lengths, which would help to clarify this situation, are not feasible with present apparatus.

[11] P. Doty, *Coll. Czechoslov. Chem. Commun.*, **22**, Spec. Issue, 5 (1957).

[12] Fellow of the National Foundation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON
STEVEN B. ZIMMERMAN[12]
JOHN A. SCHELLMAN

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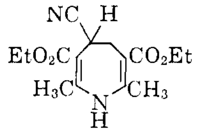
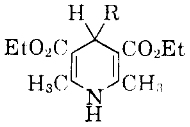
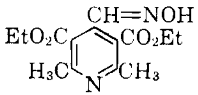
2.7-DIMETHYLAZATROPONE-4

Sir:

We recently described the ring-expansion of II, R = CH_2Cl, to diethyl 2,7-dimethyl-4-cyano-4,5-dihydro-1H-azepine-3,6-dicarboxylate, I.[1] During dehydrogenation studies, we treated I, as well as several dihydropyridines, with sodium nitrite in glacial acetic acid.[2] Some dihydropyridines (*e.g.*, II, R = CH_3) gave the expected pyridine derivatives but II, R = CH_2Cl, yielded the oxime, III (analysis, ultraviolet, infrared and n.m.r. spectra and formation of benzoate) and I afforded a white crystalline solid (15.8%), $C_{14}H_{17}NO_5$, m.p. 119–120° ($\lambda_{\max}^{\mathrm{EtOH}}$ 219 (ϵ 35,600), 249 (infl. ϵ 11,400) and 296 mμ (ϵ 9,400)) which had no NH stretching band in the infrared. The n.m.r. spectrum[3] of this compound (in $CHCl_3$ solution) showed that it had two non-equivalent ethyl esters, two methyl groups (7.07, 7.17 τ) and one other single proton (1.25 τ). These signals are all shifted to low field relative to starting material and together with the position of absorption of the single proton, suggest a ring current and hence aromaticity[4] of this product, which we believe, therefore, to be IV, R = COOEt. Compound IV, R = COOEt, now has been obtained directly from II, R = CH_2Cl, by prolonged treatment with aqueous ethanolic potassium cyanide (0.5 mole KCN/mole II, R = CH_2Cl), and chromatography of the oily product on alumina.


I


II


III


IV

Hydrolysis of IV, R = COOEt, with caustic soda yielded a diacid (94%) which was decarboxylated with copper bronze at 320°[5] to give a colorless liquid (85%), C_8H_9NO, ($\lambda_{\max}^{\mathrm{EtOH}}$ 217 (ϵ 13,370), 250 (ϵ 6,450), 257 (ϵ 5,920) and 290 mμ (ϵ 8,790)), showing no NH stretching band in the infrared but having strong absorption at 1613 cm.$^{-1}$ which we ascribe to the "carbonyl" frequency.[6] This product gave a crystalline picrate,[7] m.p. 128° (dec.). The n.m.r. spectrum (in CH_2Cl_2) of this decarboxylated material showed the presence of two methyl groups (7.41, 7.53 τ) and three other protons [2.36, 3.02 (doublet, J = 7.9 c.p.s.) and 3.69 τ] and this is consistent with structure IV, R = H. There appeared to be no "meta" or "para" interaction[8] between the ring protons, but the signal at 3.69 τ was a close quartet, J = 0.8 c.p.s., clearly by interaction with the higher field methyl group (a doublet, J = 0.8 c.p.s.).

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[2] E. Benary and G. Löwenthal, *Ber.*, **55**, 3429 (1922).

[3] Determined at 60 Mc./sec. on an A.E.I. RS 2 instrument with tetramethylsilane as internal reference.

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[8] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

[9] Department of Chemistry, University of California, Berkeley 4, California.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY, NOTTINGHAM
ENGLAND
E. BULLOCK
B. GREGORY
A. W. JOHNSON[9]

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NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME HYPOFLUORITES

Sir:

The n.m.r. spectra of F_2, OF_2, CF_3OF, SF_5OF, and SO_3F_2 were taken to see how the hypofluorite resonances of the hypofluorites compared with elemental fluorine and with each other. At the same time it was desirable to observe coupling constants between different types of fluorine atoms in the hypofluorites and to gain additional information concerning molecular structure.

In Table I is presented the order into which the n.m.r. resonances of the hypofluorite fluorine atoms of the hypofluorites fall along with the various coupling constants and chemical shifts observed. Sulfur hexafluoride, because of its ready availability and its ability to dissolve all substances mentioned here, was chosen as internal reference. The data suggest that the charge of fluorine in the –OF group is not positive, but instead, somewhat negative.