

largest difference between the two sets of chemical shift data is 0.05 p.p.m., in agreement with Diehl and Liepert's observations on small molecules.

The situation is more complicated in the case of deuteriochlorophyll, for the presence of magnesium and the phytol chain affects the correlation time, and this should make a substantial difference in the d.m.r. spectrum. We have therefore measured the d.m.r. spectrum of chlorophyll *a*- d_{72} in 50% tetrahydrofuran-chloroform- d_1 (v./v.). The natural line width is increased by the phytol chain and the magnesium to the extent that the methyl resonances are no longer fully resolved, but the chemical shift values for the envelope of resonances are directly comparable with the chemical shifts of the ring methyl groups in solutions of monomeric chlorophyll *a*. The phytol deuterium resonances, however, surprisingly exhibit a very considerable upfield shift. The strongest peak in the deuterium phytol resonance (6.95 p.p.m. upfield from CDCl_3) corresponds to a chemical shift of 0.83 p.p.m. in hydrogen phytol, and is fully 0.63 p.p.m. higher in field than the terminal methyl groups in either ordinary phytol or the phytol of chlorophyll.⁷ The minor changes in the chemical shift of the low-field methyl groups rule out the possibility that the change in the deuterium phytol shift is caused by changes in the bulk properties of the solution. Although the d.m.r. shift may arise from differences in the association of the phytol chain in deuteriochlorophyll with the porphyrin ring as compared to the situation in ordinary chlorophyll, and large shifts in proton resonances occur in chlorophyll as a function of aggregation,⁶ we prefer at this time to attribute the difference in chemical shift to deuterium isotope effects.

Nucleus-electron interactions and primary isotope effects on local electron density may be important factors in the d.m.r. shifts as in other isotope effects. We believe that differences in electronic properties between bonds to hydrogen and bonds to deuterium may be correlated, not with differences in infrared vibrational frequencies, but with differences in infrared absorption peak intensities.⁸ Bonds to hydrogen and corresponding bonds to deuterium may have very different intensities in the infrared.¹¹ Since the absolute intensity is related to variations of the dipolar moment of a C-H bond by $|A| = N\pi/3c(\partial\mu/\partial Q)^2$, the generally smaller values of $|A|$ for C-D bonds suggest a smaller value of $(\partial\mu/\partial Q)$, and a higher value for the electron density near a deuterium atom. Deuterium should thus experience an upfield shift relative to protium, and an adjacent proton should experience an upfield shift also. Since n.m.r. shifts measure only the differences in shielding for different chemical species, the close agreement of the ^1H and ^2H chemical shifts in Table I

(7) The chemical identity of ordinary and deuteriochlorophylls is established by their chromatographic behavior.

(8) Jouve, *et al.*,⁹ have shown a good correlation between the absolute intensity of an infrared absorption peak and chemical shifts in proton magnetic resonance. Such a correlation is not surprising in the light of well-recognized relations between infrared band intensities and substituent effects.¹⁰

(9) P. Jouve, M. Teulier, and G. Levi, *Compt. rend.*, [9] **258**, 2545 (1964).

(10) Cf. T. L. Brown, *J. Phys. Chem.*, **64**, 1798 (1960); D. Hadži in "Infrared Spectroscopy and Molecular Structure," M. Davies, Ed., Elsevier Publishing Co., Amsterdam, 1963, Chapter VII, pp. 249-257.

(11) See, for example, R. M. Adams and J. J. Katz, *J. Opt. Soc. Am.*, **46**, 895 (1956); H. H. Strain, M. R. Thomas, H. L. Crespi, and J. J. Katz, *Biochem. Biophys. Acta*, **52**, 517 (1961).

is not surprising. Although the mechanism is not entirely clear, it appears qualitatively that an integrated isotope effect may suffice to account for the observed differences in the chemical shift of hydrogen and deuterium in the phytol residue.

The solvent dependence of the chlorophyll *a*- d_{72} d.m.r. spectrum has also been examined, and the line width is found to be highly dependent on the aggregation state of the chlorophyll.⁶

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Reactions of the 2-Halo-3-(2-hydroxyethoxy)cyclohexenes with Potassium *t*-Butoxide in Dimethyl Sulfoxide¹

Sir:

As part of a program directed toward determining the scope and limitations of reactions of 2-haloallyl compounds with base,² we prepared the 2-halo-3-(2-hydroxyethoxy)cyclohexenes **1** and **2** and studied their reactions with potassium *t*-butoxide in dimethyl sulfoxide (DMSO). Our results show that cyclohexenyl halides can undergo reactions with strong base by mechanisms other than those involving cyclohexenes.³

Using procedures similar to that described for the preparation of 2-bromoallyloxyethanol,^{2a} 2-bromo-3-(2-hydroxyethoxy)cyclohexene (**1**),⁴ b.p. 96° (1 mm.), n_D^{20} 1.5222, and its chloro analog **2**,⁴ b.p. 108° (5 mm.), n_D^{20} 1.4962, were prepared in >50% yield from the corresponding 2,3-dihalocyclohexene^{5,6} and sodium ethylene glycolate in ethylene glycol. Treatment of **1** with 2.2 equiv. of 1.23 *M* potassium *t*-butoxide in DMSO at 60° for 6 hr. gave a 71% yield of a mixture of two compounds, **3** and **4**, b.p. 51° (2 mm.), in nearly equal amounts. Similar treatment of **2** gave a 42% yield of a mixture that was 8% **3** and 92% **4**. The components were separated by gas chromatography (20% Carbowax 20M on alkaline firebrick at 162°), and **3**,⁴ n_D^{20} 1.4764, was found to have infrared and n.m.r. spectra that were indistinguishable from those of cyclohex-2-enone ethylene ketal⁴ prepared from cyclohex-2-enone⁷ and ethylene glycol.⁸ Spectral and

(1) (a) Supported by Grant No. GM-10606 from the National Institute of General Medical Sciences, U. S. Public Health Service; (b) abstracted from the Ph.D. Thesis of W. Schear, University of California, Davis, 1965.

(2) (a) A. T. Bottini, F. P. Corson, and E. F. Böttner, *J. Org. Chem.*, **30**, 2988 (1965); (b) A. T. Bottini, J. A. Mullikin, and C. J. Morris, *ibid.*, **29**, 373 (1964); (c) A. T. Bottini and E. F. Böttner, *ibid.*, in press.

(3) See L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1917 (1965).

(4) The experimental and theoretical carbon and hydrogen analyses agreed to within 0.3%, and the infrared and 60-Mc. n.m.r. spectra were compatible with the assigned structure.

(5) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962).

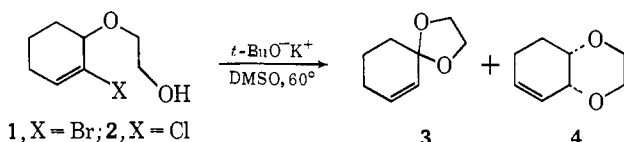
(6) E. Bergman, *ibid.*, **28**, 2210 (1963).

(7) F. C. Whitmore and G. W. Pedlow, Jr., *J. Am. Chem. Soc.*, **63**, 758 (1941).

(8) For the method used, see R. F. Fischer and C. W. Smith, *J. Org. Chem.*, **25**, 319 (1960). Acid hydrolysis of **3** gave cyclohex-2-enone (2,4-dinitrophenylhydrazone, m.p. 163.5-165.5°) and ethylene glycol (*p*-nitrophenylurethan, m.p. 128-132°). **3** has also been prepared by dehydrohalogenation of the 2-halocyclohexanone ethylene ketals.⁹

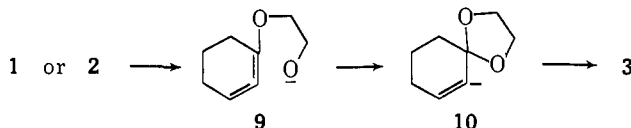
(9) H. W. Wanzlich, G. Gollman, and H. Milz, *Chem. Ber.*, **88**, 69 (1955).

analytical data for **4**,¹⁰ $n^{24}D$ 1.4702, showed that (1) it was isomeric with **3** (Anal. Found: C, 68.68; H, 8.44), (2) it possessed no hydroxyl function (no band in the 3350-cm.⁻¹ region), and (3) it possessed two vinyl hydrogens (n.m.r.) attached to a nonpolar double bond (λ 1650 cm.⁻¹, m). Unlike **3**, **4** was not destroyed by treatment with dilute acid. Further, hydrogenation of **4** over palladium on charcoal gave *cis*-2,5-dioxabicyclo[4.4.0]decane (**5**).^{4,11} The results indicated that **4** was either *cis*-2,5-dioxabicyclo[4.4.0]dec-7-ene or its 8-ene isomer (**8**). As its 60-Mc. n.m.r. spectrum, multiplets at 382–350 (2 H), 274–228 (6 H), and 162–130 (4 H) c.p.s., was considerably more complex than would be expected for **8**, the 7-ene structure was as-

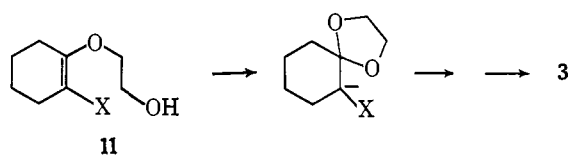


signed to **4**.

Formation of **3** is best explained as occurring by a mechanism in which the first step is dehydrohalogenation of **1** or **2** to give the cyclohexa-1,2-diene **9**; **9** can then undergo nucleophilic addition of alkoxide to form the anion **10**, which abstracts a proton to form **3**. Significantly, the course of ring closure of **9** is the same as that observed for 2-(allenloxy)ethanol^{2a} and 3-(allenloxy)propanol,^{2c} which give acrolein ethylene ketal and acrolein trimethylene ketal, respectively.



Another plausible mechanism that can be pictured for formation of **3** is an addition-elimination mechanism involving the corresponding 2-halo-3-(2-hydroxyethoxy)cyclohexene (**11**), which conceivably could be



formed by prototropic rearrangement of **1** or **2**. However, such a mechanism seems untenable because 3-isopropoxycyclohexene (**12**),⁴ b.p. 79 (92 mm.), $n^{24}D$ 1.4448 (from 3-bromocyclohexene and isopropyl alcohol), is not converted to 1-isopropoxycyclohexene (**13**) under the reaction conditions.¹⁸ Note that failure to observe conversion of a 3-alkoxycyclohexene to a 1-alkoxycyclohexene is not the result of an equilibrium that favors the former; treatment of 1-ethoxycyclo-

(10) Gas chromatography of **4** on a 150-ft. capillary column [1,2,3-tris(2-cyanoethoxy)propane at 142°] gave a single elution band.

(11) The *trans* isomer of **5** (**6**) was prepared in poor yield by treatment of *trans*-1,2-cyclohexanediol with ethylene bromide and copper powder using conditions similar to those described for the preparation of benzo[1,4]dioxane (**7**).¹² Hydrogenation of **7** over platinum oxide gave a mixture, b.p. 89° (13 mm.), of both **5**, $n^{25}D$ 1.4731, and **6**, $n^{25}D$ 1.4671, which was separated by gas chromatography [silicone SF-96 on Chromosorb W-HMDS at 138°].

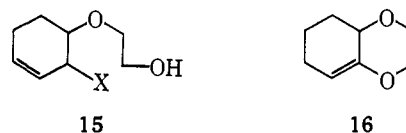
(12) B. N. Ghosh, *J. Chem. Soc.*, 107, 1588 (1915).

(13) In this regard, see T. J. Prosser, *J. Am. Chem. Soc.*, 83, 1701 (1961); C. C. Price and W. H. Snyder, *ibid.*, 83, 1773 (1961).

hexene,¹⁴ b.p. 60° (19 mm.), $n^{24.5}D$ 1.4537, with 0.54 *M* potassium *t*-butoxide in DMSO gave no rearranged ether.

Although no **12** was converted to **13** on treatment with 0.54 *M* potassium *t*-butoxide in DMSO, **12** was converted slowly to 4-isopropoxycyclohexene (**14**)⁴; after 6 hr. at 65°, **12** gave a 60:40 mixture of **12** and **14**, which was separated by gas chromatography (cyanosilicone XF-1150 on Chromosorb W-HMDS at 100°).

Rearrangement of **12** to **14** indicates that the first step of the mechanism by which **1** and **2** are converted to **4** is prototropic rearrangement to the 3-halo-4-(2-hydroxyethoxy)cyclohexene (**15**). It can be expected that such rearrangement will give as the main product the more stable *trans*-**15**, which will give **4** by an intramolecular SN reaction.



Significantly, no 2,4-dioxabicyclo[4.4.0]dec-6-ene (**16**), the expected cyclization product of 3-(2-hydroxyethoxy)cyclohexene, was observed as a product from the reactions of **1** and **2**. Although **16** could have been formed and converted to **4** or other products, we consider this unlikely because of the observed stability of **13** and because we can see no good reason why conversion of **16** to **4** should be stereospecific.

(14) A. Johannissian and E. Akunian, *Bull. Univ. État RRS Arménie*, No. 5, 245 (1930); *Chem. Abstr.*, 25, 921 (1931).

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Fluoride Complexes of Pentavalent Plutonium¹

Sir:

We wish to announce the preparation of compounds containing pentavalent plutonium, Rb_2PuF_7 and $CsPuF_6$. The compounds are the first fluoride complexes to be characterized in which a transuranium element in the pentavalent state occurs without the "yl" type of oxygen bonding.

Although PuF_3 , PuF_4 , and PuF_6 are well-known compounds, the evidence for PuF_5 is vague and contradictory.² As a solution species, PuO_2^+ is very unstable in fluoride, disproportionating into Pu(IV) and Pu(VI). Recent experience in the stabilization of U(V) by fluoride ion and in the formation of numerous alkali-uranium(V) and alkali-protactinium(V) fluoride complexes^{3,4} led us to examine the plutonium system in the hope that an analogous salt of pentavalent plutonium might be formed.

Of necessity a different approach for plutonium was taken than in the case of uranium where UF_5 could be

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter VII.

(3) G. D. Sturgeon, R. A. Penneman, F. H. Kruse, and L. B. Asprey, *Inorg. Chem.*, 4, 748 (1965).

(4) L. B. Asprey and R. A. Penneman, *Science*, 145, 924 (1964).