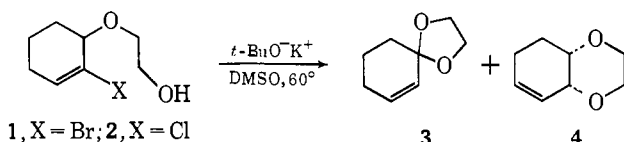
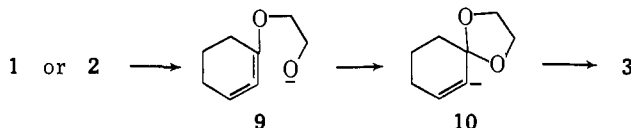


analytical data for **4**,¹⁰ n^{24}_D 1.4702, showed that (1) it was isomeric with **3** (Anal. Found: C, 68.68; H, 8.44), (2) it possessed no hydroxyl function (no band in the 3350-cm.⁻¹ region), and (3) it possessed two vinyl hydrogens (n.m.r.) attached to a nonpolar double bond (λ 1650 cm.⁻¹, m). 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-

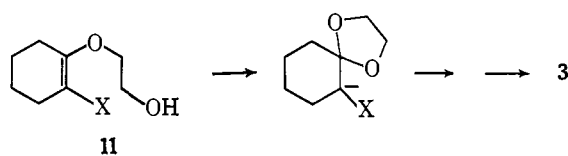


signed to **4**.

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.¹³ 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°].

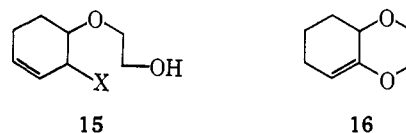
(12) B. N. Ghosh, *J. Chem. Soc.*, **107**, 1588 (1915).

(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).

used as the starting material; we used fluorine gas as the oxidant, starting with compounds containing plutonium in the tetravalent state. A successful procedure was as follows.

Rubidium carbonate (in the 2:1 mole ratio of Rb:Pu) was added to a solution of Pu(IV) nitrate in a platinum dish and was acidified with HF. The contents of the dish were evaporated to dryness and ground in a mortar to give a pale pink powder. The X-ray powder pattern of this tetravalent plutonium starting material showed rhombohedral $7\text{RbF} \cdot 6\text{PuF}_4$ as the major phase plus some unidentified material. This mixture was placed in a sapphire dish in a nickel fluorinator and heated with fluorine gas (1 to 1.5 atm. of F_2 at 300–400° for 4–16 hr.).

The product was an intense green salt with no residual traces of pink color. X-Ray powder analysis gave a new pattern, free from lines of the starting material. This pattern was indexed as monoclinic, $a_0 = 6.270$, $b_0 = 13.416$, $c_0 = 8.844$ (all ± 0.008 Å.), and $\beta = 90^\circ$. Rb_2PuF_7 is isostructural with analogous compounds of pentavalent uranium,⁵ Rb_2UF_7 ; niobium,^{6,7} K_2NbF_7 ; and tantalum,⁷ K_2TaF_7 . In Table I, several of the most intense lines are given for Rb_2PuF_7 along with the calculated values.

Table I. Partial X-Ray Powder Pattern Data for Rb_2PuF_7 , P_{21}/c

<i>hkl</i>	<i>d</i> , Å.		<i>I</i>	
	Calcd.	Obsd.	Calcd.	Estd.
110	5.680	5.67	53	60
021	5.353	5.35	91	80
111	4.786	4.78	44	50
002	4.442	4.46	43	45
130	3.641	3.63	87	100
102	3.625		39	
112	3.499	3.50	100	80
131	3.369	3.37	72	75
200	3.135	3.137	40	60
061	2.168	2.168	28	40
223, 161	2.050	2.04 Br	32	60
242	2.036		26	
261	1.783		23	

Cesium plutonium(IV) fluoride (1:1 mole ratio Cs:Pu) was fluorinated at 350° overnight. The product was CsPuF_6 , isostructural⁵ with rhombohedral CsUF_6 , but not with CsPaF_6 or RbPaF_6 , which are orthorhombic.⁸ The compound had a unique absorption spectrum unlike that of Pu(III), Pu(IV), or Pu(VI). The pentavalent plutonium complex gradually altered after several days forming CsPuF_5 identified by X-ray; absorption spectrophotometry showed both Pu(IV) and Pu(VI) to be present. Titration of iodine liberated from a freshly prepared sample of CsPuF_6 showed that >90% of the plutonium was in the pentavalent state.

(5) R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

(6) G. M. Brown and L. A. Walker, Oak Ridge National Laboratory (neutron diffraction of K_2NbF_7), submitted for publication.

(7) J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939).

(8) L. B. Asprey, F. H. Kruse, and R. A. Penneman, submitted for publication.

R. A. Penneman, George D. Sturgeon
L. B. Asprey, F. H. Kruse

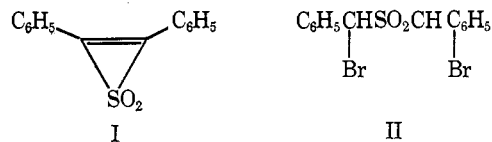
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2,3-Diphenylvinylene Sulfone

Sir:

We wish to report the synthesis of 2,3-diphenylvinylene sulfone (I), the first example of a three-membered ring heterocycle which is potentially aromatic because of the possible involvement of d orbitals at the hetero atom.¹ Application of the Ramberg–Bäcklund reaction^{4,5} to α, α' -dibromodibenzyl sulfone (II) using triethylamine in methylene dichloride gave in 70% yield the



unusual sulfone I, m.p. 116–126° dec.^{8,9} The precursor dibromo sulfone II, m.p. 162–164°, was obtained in 30–35% yield, without the isolation of intermediates, by oxidation of α, α' -diphenylthiodiglycolic acid (III)¹¹ by means of hydrogen peroxide followed by brominative decarboxylation¹² of the resulting crude α, α' -diphenylsulfobisacetic acid (IV). The ultraviolet spectrum



$[\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}} \mu\text{m} (\log \epsilon)]$ 222.5 (4.26), 296 (4.34), 307 (4.41), and 322 (4.27)] of the sulfone (I) shows marked similarity to the spectra of compounds incorporating the 1,2-diphenylcyclopropene chromophore,¹³ such as 1,2-diphenylcyclopropene-3-carboxylic acid. The infrared spectrum shows several strong bands in the regions generally associated with the asymmetric and symmetric stretching modes of the SO_2 group.¹⁴ The two most intense peaks appear at 7.82 and 8.57 μ in carbon tetrachloride solution.¹⁵ The presence of the conjugated

(1) Volpin and co-workers [M. E. Volpin, Y. D. Koresnikov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962)] have recently tabulated a number of such systems and in addition claimed the synthesis of appropriate silicon and germanium derivatives which however were subsequently shown to be dimeric.^{2,3}

(2) F. Johnson and R. S. Gohlke, *Tetrahedron Letters*, 1291 (1962).

(3) R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963).

(4) L. Ramberg and B. Bäcklund, *Arkiv Kemi Mineral. Geol.*, **13A**, No. 27, 1 (1940); *Chem. Abstr.*, **34**, 4725 (1940).

(5) Although episulfones have long been considered to be involved in the Ramberg–Bäcklund reaction, this is the first time that an intermediate with an intact three-membered ring has been isolated. This work therefore provides strong support for the commonly accepted mechanism of the Ramberg–Bäcklund reaction advanced by Bordwell and co-workers.^{6,7}

(6) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).

(7) N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963).

(8) The decomposition point varies markedly with the rate of heating.

(9) *Anal.* Calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}$: C, 69.40; H, 4.17; S, 13.23; mol. wt., 242. Found: C, 69.62, 69.70; H, 4.11, 4.28; S, 13.18; 13.25; mol. wt.,¹⁰ 245, 253.

Acceptable C, H, and S analyses and consistent spectral data were also obtained for all other new compounds prepared in the course of this work.

(10) By means of vapor osmometry in chloroform and benzene, respectively.

(11) T. Mazonski and B. Prajsnar, *Zeszyty Nauk Politech. Slask. Chem.*, No. 7 17 (1961); *Chem. Abstr.*, **62**, 13079d (1965).

(12) A modification of the method of W. M. Ziegler and R. Connor [*J. Am. Chem. Soc.*, **62**, 2596 (1940)] was used.

(13) R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

(14) (a) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949); (b) L. J. Bellamy and R. L. Williams, *ibid.*, 863 (1957);

(c) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961); (d) P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochim. Acta.*, **16**, 1312 (1960);

(e) O. Exner, *Collection Czech. Chem. Commun.*, **28**, 935 (1963).