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 $7RbF \cdot 6PuF_4$ 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 $\pm 0.008$ Å.), and $\beta = 90°$. $Rb_2PuF_7$ 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 $Rb_2PuF_7$, $P2_1/c$

| | d, Å. | | I | |
|---|---|---|---|---|
| *hkl* | 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 | 1.784 | 23 | 50 |

Cesium plutonium(IV) fluoride (1:1 mole ratio Cs:Pu) was fluorinated at 350° overnight. The product was $CsPuF_6$, isostructural[5] 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.

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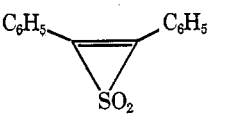
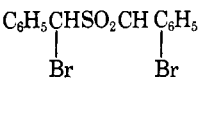
## 2,3-Diphenylvinylene Sulfone

*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

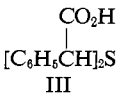


I

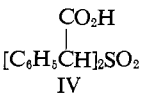


II

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 decarboxylation[12] of the resulting crude α,α′-diphenylsulfobisacetic acid (IV). The ultraviolet spectrum



III



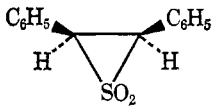
IV

[$\lambda_{max}^{C_2H_5OH}$ mμ (log ε) 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. Koreshkov, 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 coworkers.[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 $C_{14}H_{10}O_2S$: 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**, 13079*d* (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).

double bond, which is clearly revealed in the ultraviolet spectrum, could not be unequivocally identified in the infrared spectrum presumably because of interfering phenyl absorption.[17] The n.m.r. spectrum of I exhibits only a complex multiplet centered at $\delta$ 7.55 due to the aromatic protons.

At its melting point smooth decomposition of I occurs with the formation of diphenylacetylene (72%) and sulfur dioxide. Firm evidence for the presence of



V

the three-membered ring in sulfone I was obtained by reduction of the double bond by means of aluminum amalgam[18] at $-45$ to $-40°$ in wet ether containing 0.5% ethanol. This gave the corresponding *cis*-episulfone (V),[19] m.p. 85–88° dec., in 8% yield (16% based on recovered I). For purposes of comparison the episulfone V was prepared in 49% yield by a well-known general method[7,20,21] involving treatment of phenyldiazomethane with sulfur dioxide at $-30°$. The stereochemistry of V is assigned on the basis[7] of its decomposition at the melting point to *cis*-stilbene (83%).

Although the question of the possible aromatic stabilization of the vinylene sulfones must await further work now in progress on I as well as on the parent heterocycle and its alkyl and other aryl derivatives, it is striking that the unsaturated sulfone I is remarkably more stable than the saturated analog V. Solutions of V in chloroform at room temperature rapidly developed the odor of sulfur dioxide, and infrared examination showed that in 1–2 days most of the sulfone had undergone conversion to *cis*-stilbene. On the other hand the unsaturated sulfone I appeared to be stable for at least 2 months in chloroform solution at room temperature and in fact could be recrystallized easily from hot benzene.

*Acknowledgment.* Thanks are due to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U. S. Army Research Office, Durham, for partial support of this work.

(15) These tentative assignments are based on the shifts to longer wavelengths (7.91 and 8.62 $\mu$, respectively) which are observed in chloroform solution.[14a,16] The band at 7.82 $\mu$ is somewhat outside the range normally quoted[14] for the asymmetric stretching mode, but a less intense band at 7.57 $\mu$, which falls more closely on the Bellamy–Williams internal correlation line,[14b,c] is insensitive to solvent or phase change (carbon tetrachloride, chloroform, Nujol mull, KBr pellet).

(16) S. Ghersetti, *Boll. sci. chim. ind. Bologna*, **21**, 237 (1963).

(17) On the other hand a number of acyclic, phenylated $\alpha,\beta$-unsaturated sulfones show a moderately intense band at 6.15 $\mu$ due to the conjugated double bond.

(18) F. L. Hahn and E. Thieler, *Ber.*, **57**, 671 (1924).

(19) In contrast to the case of I the infrared spectrum of V shows only two intense bands in the regions normally associated with the $SO_2$ bands: $\lambda_{max}^{CCl_4}$ 7.43 and 8.62 $\mu$; $\lambda_{max}^{CHCl_3}$ 7.49 and 8.67 $\mu$.

(20) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

(21) G. Hesse and S. Majmudar, *ibid.*, 93, 1129 (1960).

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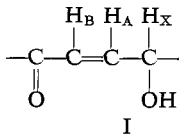
## The Isolation and Structural Elucidation of a Novel Steroidal Tumor Inhibitor from *Acnistus arborescens*[1,2]

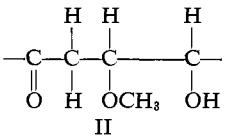
*Sir:*

The leaves of *Acnistus arborescens* (L.) Schlecht (Solanaceae) and related species have been used for many years to treat cancerous growths.[3] During our search for tumor inhibitors from plant sources, alcoholic extracts of dried *A. arborescens* leaves[4] showed significant inhibitory activity when tested *in vitro* against cells derived from human carcinoma of the nasopharynx (KB) and *in vivo* against sarcoma 180 in mice.[5] We report herein the isolation and structural elucidation of a novel steroidal tumor inhibitor from *A. arborescens*.

Fractionation of the ethanol extract, guided by assay against sarcoma 180, revealed that the active principle was concentrated, successively, in the chloroform layer of a chloroform–water partition, in the aqueous methanol layer of a 10% aqueous methanol–petroleum ether partition, and in the chloroform layer of a 45% aqueous methanol–chloroform partition. Further fractionation involving alumina chromatography yielded compound A,[6] $C_{28}H_{38}O_6$, m.p. 252–253°, $[\alpha]^{28}D$ +125°,[7] which shows $\lambda_{max}^{alc}$ 214 m$\mu$ ($\epsilon$ 17,300), $\lambda_{max}$ 2.81, 2.94, and 5.92 $\mu$ (broad), and n.m.r. signals at $\tau$ 3.05 ($H_A$, quartet, $J_{AB}$ = 10 c.p.s., $J_{AX}$ = 6 c.p.s.), 3.82 ($H_B$, doublet, $J_{AB}$ = 10 c.p.s.), 6.25 ($H_X$, doublet, $J_{AX}$ = 6 c.p.s.) for the ABX system of I, 5.64 (2 H, $=CCH_2OH$), 6.78 (1 H, epoxy H), 7.95 (3 H, $-C{=}CCH_3$), 8.58 and 9.28 (6 H, two tertiary $CH_3$), and 9.02 (3 H, doublet, $J$ = 7 c.p.s., one secondary $CH_3$). Compound A was



I



II

converted to several crystalline derivatives: the diacetate, $C_{32}H_{42}O_8$, m.p. 201–202°, $[\alpha]^{30}D$ +192°, $\lambda_{max}^{alc}$ 214 m$\mu$ ($\epsilon$ 18,000), $\lambda_{max}$ 5.76 (acetate ester), 5.86 ($\alpha,\beta$-unsaturated $\delta$-lactone), and 5.94 $\mu$ ($\alpha,\beta$-unsaturated ketone); the tetrahydrodesoxy derivative (by hydrogenation with hydrogen and palladium), $C_{28}H_{42}O_5$, m.p 228–229°, $\lambda_{max}$ 2.79, 5.78 ($\delta$-lactone), and 5.86 $\mu$ (ketone); the methanol adduct, $C_{28}H_{42}O_7$, m.p. 242–243°, $[\alpha]^{35}D$ +19°, $\lambda_{max}^{alc}$ 217 ($\epsilon$ 9500), $\lambda_{max}$ 2.79, 2.94, 5.86 ($\alpha,\beta$-unsaturated $\delta$-lactone), and 5.91 $\mu$ (ketone), n.m.r. spectrum showing the presence of a methoxyl

(1) Tumor Inhibitors. XIV. Part XIII in the series: S. M. Kupchan, S. J. Barboutis, J. R. Knox, and C. A. Lau Cam, *Science*, in press.

(2) This investigation was supported by grants from the National Cancer Institute (CY-04500) and the American Cancer Society (T-275).

(3) R. de Grosourdy, "El Médico Botànico Criollo," F. Brachet, Paris, 1864; F. Haüssler, *Schweiz. Apoth.-Ztg.*, **52**, 260, 275 (1914). We thank Dr. Jonathan L. Hartwell of the National Cancer Institute for calling these references to our attention.

(4) The plant material was collected by J. A. S. R. in Costa Rica in Jan. 1961.

(5) Cytotoxicity and *in vivo* inhibitory activity were assayed, under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, by the procedures described in *Cancer Chemotherapy Rept.*, **25**, 1 (1962).

(6) Compound A showed significant inhibitory activity against sarcoma 180 in mice at 20 mg./kg., and cytotoxicity ($ED_{50}$) against KB cell culture at 0.15 $\mu$g./ml.[5]

(7) All rotations and infrared spectra are in chloroform, unless otherwise noted. N.m.r. spectra were determined on a Varian Associates A-60 spectrometer in deuteriochloroform; chemical shifts are reported in $\tau$ values (p.p.m.). Satisfactory analyses have been obtained for products with cited empirical formulas.