cerning the mechanistic pathway connecting R^+ and the *endo* isomer. Presumably the classical ion is an intermediate in this step.[2-5] It seems likely that the barrier for capture of the nonclassical ion is larger than that for capture of the less stable classical ion, in which case ΔE_a represents a lower limit for the energy difference of the classical and nonclassical ions.

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Received April 26, 1965

Alkali Fluoride Complexes of Tetravalent Protactinium

Sir:

We wish to report the first preparation of alkali fluoride complexes of *tetravalent protactinium.* The compounds were prepared by two methods: (1) vacuum heating of PaF_4 with alkali fluoride, and (2) hydrogen reduction of pentavalent protactinium compounds, which was the method yielding purer preparations. Compounds of tetravalent protactinium were obtained which are isostructural with known compounds of tetravalent uranium. In fluorine, the tetravalent protactinium compounds are oxidized to the starting compounds of pentavalent protactinium, identified by their own characteristic X-ray powder patterns. This hydrogen reduction–fluorine oxidation cycle can be repeated. Although a number of fluoride complexes of *pentavalent* protactinium are known, *e.g.*, K_2PaF_7,[2] $MPaF_6$ (M = NH_4, K, and Rb),[3] and Na_3PaF_8,[4] no fluoride complexes of *tetravalent* protactinium have been reported previously.

In our recent studies of MXF_6 compounds (X = U or Pa; M = alkali)[3,5] it was shown that $RbUF_6$ and $RbPaF_6$ are isostructural; more recent single crystal measurements have established their structure as orthorhombic.[6] In the review of the alkali fluoride–uranium tetrafluoride systems by Thoma,[7] it was shown that rhombohedral compounds of the type $7MF \cdot 6UF_4$ occur frequently, and a prediction of this structure for the then unknown compound $7RbF \cdot 6PaF_4$ was made. Thus, X-ray powder techniques offered an excellent method of establishing both the reduction of protactinium(V) fluoride complexes to protactinium(IV) compounds and also the reverse reaction.

The chemistry of the conversion was investigated as follows. Into a depression ground in a sapphire dish was placed a few milligrams of RbF and $\cdot PaF_4$ in the mole ratio Rb:Pa = 7:6. Into another sapphire dish was placed crystalline $RbF \cdot PaF_5$ prepared as previously described.[3] Both materials were heated in a fluorine atmosphere (1–1.2 atm.) for ~2 hr. at 390°. X-Ray powder patterns established that $RbF \cdot PaF_5$ was the only phase detectable in each sample. Without removal from the sapphire dishes, they were then exposed to very pure hydrogen (made from UH_3) for 4 hr. at 450°. The X-ray powder patterns of the reduction products showed that rhombohedral $7RbF \cdot 6PaF_4$ was the major phase in each case; it was isostructural with $7RbF \cdot 6UF_4$. Treatment with fluorine oxidized both samples to the original orthorhombic $RbPaF_6$ phase. Hydrogen reduction again formed the rhombohedral protactinium(IV) compound.

Identification of the tetravalent protactinium compound was accomplished by comparison with our X-ray data[8] for rhombohedral $7NH_4F \cdot 6UF_4$ and with the $7RbF \cdot 6UF_4$ data listed by Brunton, *et al.*[9] A partial list of the indexed X-ray powder pattern data for $7RbF \cdot 6PaF_4$ is given in Table I.

Table I.[a] X-Ray Powder Pattern Data for $7RbF \cdot 6PaF_4$

hkl	I/I_0	d_{obsd}, Å.	d_{calcd}, Å.
101	7	8.36	8.32
110	2	7.73	7.71
021	3	5.65	5.66
012	4	4.98	4.94
211	4	4.58	4.56
300	3	4.45	4.45
202	2	4.18	4.16
220	2	3.85	3.86
122	2	3.70	3.66
221	2	3.58	3.58[b]
003	10	3.51	3.54
131			3.50

[a] Cu Kα radiation, Debye–Scherrer camera, 114.6 mm., Ilford "G" film; hexagonal indices, space group R3-C_{3i}^2; a_0 = 15.43, c_0 = 10.63 Å. (rhombohedral, a_0 = 9.587 A., α = 107° 9′).
[b] This line appears in typical patterns; not indexable in R$\bar{3}$.

Further work with the remaining alkali and ammonium fluorides is in progress.

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] A. V. Grosse, *J. Am. Chem. Soc.*, **56**, 2501 (1934); *Proc. Roy. Soc.* (London), **A150**, 363 (1935).

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

[4] D. Brown and J. E. Easey, *Nature*, **205**, 589 (1965).

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

[6] L. B. Asprey, F. H. Kruse, and R. A. Penneman, manuscript in preparation.

[7] R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

[8] R. Benz, R. M. Douglass, F. H. Kruse, and R. A. Penneman, *ibid.*, **2**, 799 (1963).

[9] G. D. Brunton, H. Insley, T. M. McVay, and R. E. Thoma, ORNL-3761, Feb. 1965.

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σ-Overlap of p-Orbitals in Cyclic π-Electron Systems. *cis,cis,cis*-1,5,9-Cyclododecatriene

Sir:

Recently investigated[1a-g] *cis,cis,cis*-1,4,7-cyclononatriene (I) is a cyclic six-π-electron system wherein σ-overlap of the p-orbitals could have been significant. Whether this overlap lowers the ground-state energy below that expected for the same cyclic system composed of "isolated" double bonds remains undecided in the case of I.[1a,f,g] The important feature of this kind of system is not that the double bonds be homo-

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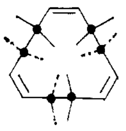
[1] (a) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963); (b) K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963); (c) *J. Mol. Spectry.*, **14**, 156 (1964). For another synthesis and other properties see (d) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); (e) W. R. Roth, *Ann.*, **671**, 10 (1964); (f) W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Am. Chem. Soc.*, **86**, 3178 (1964); (g) S. Winstein and F. P. Lossing, *ibid.*, **86**, 4485 (1964).

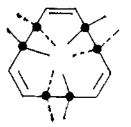
conjugated, as in I, but that the geometry be such that the lobes of the p-orbitals of any two double bonds converge and be near bonding distances. *cis,cis,cis*-1,5,9-Cyclododecatriene (II) in a crown conformation (IIa) is such a system. An HMO ($\beta' = kS'$) calculation of the energy levels of IIa (with 2,5-pp-overlap 37% that of 1,2-) predicts its delocalization energy to be 16.4% that of benzene (*cf.* values for I[1g,2]). The hydrocarbon II is the last remaining isomer of 1,5,9-cyclododecatriene to be synthesized. The all-*trans* (III) and *cis,trans,trans* (IV) isomers are commercially available and the *cis,cis,trans* (V) isomer has been reported.[3,4] We report here a synthesis and some properties of II.

IIa

IIb

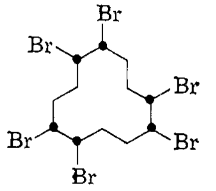


IIc

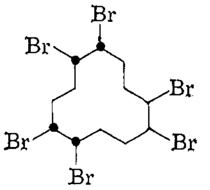


IId

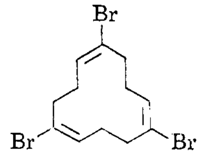
Bromination of III in acetic acid gave a hexabromide fraction (*ca.* 80%), of which *ca.* 30% is a crystalline solid, m.p. 178–179°,[5] and *ca.* 70% is an oil (column chromatographically uniform). We assign structure VI to the solid and structure VII to the oily hexabromide.



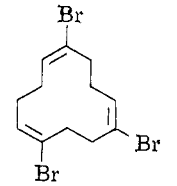
VI



VII



VIII



IX

Dehydrobromination (sodium ethoxide) of *either* VI or VII gave nearly the same mixture of two tribromocyclododecatrienes (*ca.* 90%). One, a crystalline solid (*ca.* 25%), m.p. 117°, is 1,5,9-tribromo-*cis,cis,cis*-1,5,9-cyclododecatriene (VIII)[6]; to the other, an oil, we assign structure IX.[7]

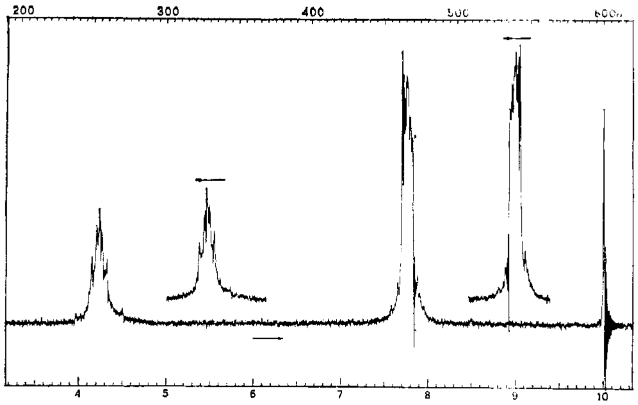


Figure 1. N.m.r. spectrum of II at 37° with tetramethylsilane as the internal reference standard (*ca.* 20% $CDCl_3$ solution).

Treatment of pure VIII, *or* a mixture of VIII and IX, with lithium, *t*-butyl alcohol, and tetrahydrofuran,[8] gave a mixture (*ca.* 95%) of two cyclododecatrienes consisting of II (*ca.* 80%) and V (*ca.* 20%). Some isomerization of a *cis* double bond occurred during this reductive step. Treatment of the mixture with silver nitrate selectively gave the complex with II (X), m.p. 150–151° dec. *Anal.* Calcd. for $C_{12}H_{18}(AgNO_3)_3$: C, 21.45; H, 2.70; Ag, 48.16. Found: C, 21.62; H, 2.79; Ag, 47.90. Addition of ammonia to X regenerated II. Extraction and distillation gave pure II (*Anal.* Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.05; H, 11.14, mol. wt., 162 (mass spectrometric determination)), m.p. −1.5°; b.p. 108° (17 mm.); $n^{24.6}\text{D}$ 1.5100; infrared (liquid film): strong absorptions at 3.32, 3.39, 3.41, 3.49, 6.80, and 13.5 μ; medium absorptions at 6.04, 6.10, 9.55, 10.1, and 12.5 μ; ultraviolet: end absorption to λ 193 mμ; λ 200 mμ (ϵ 9700) (in cyclohexane at 7.65×10^{-5} *M*); exhaustive hydrogenation gave cyclododecane identical with an authentic sample.

That the new hydrocarbon indeed is *cis,cis,cis*-1,5,9-cyclododecatriene is clear from its n.m.r. spectrum (Figure 1). The symmetrical multiplet at τ 4.23 (area 1) shows the equivalence of the olefinic hydrogens, and the multiplet at τ 7.76 (area 2) shows equivalent aliphatic hydrogens at a chemical shift characteristic for allylic hydrogens. The symmetrical multiplet at τ 7.76 must be the result of a dynamic conformational equilibration. The n.m.r. spectrum of II at *ca.* 150° showed slight changes from that obtained at 37°, whereas the spectra obtained at lower temperatures changed; the fine structure of both multiplets disappeared, giving two smooth patterns at *ca.* −80° which remained unchanged to −115° (20% in CS_2). Insolubility of II in suitable solvents prevented observation at still lower temperatures.

Of the many possible conformations for II, four are the crown (IIa), the saddle (IIb), the unsymmetrical *s-trans* (IIc), and the symmetrical *s-trans* (IId). The crown conformation, with C_{3v} symmetry, is required for

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(2) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 4061 (1963).

(3) H. Briel, P. Heimbach, M. Kröner, H. Müller, and G. Wilke, *Makromol. Chem.*, **69**, 18 (1963), and references therein.

(4) G. C. Royston, French Patent 1,353,692 (1964); *Chem. Abstr.*, **61**, 2989*b* (1964).

(5) L. I. Zakharkin and V. V. Korneva, *Dokl. Akad. Nauk SSSR*, **132**, 1078 (1960).

(6) *Anal.* Calcd. for $C_{12}H_{15}Br_3$: C, 36.12; H, 3.79; Br, 60.09; mol. wt., 398.97. Found: C, 36.27; H, 3.86; Br, 60.22; mol. wt., isotopic parent peaks *m/e*, 396, 398, 400, 402. The n.m.r. spectrum was analyzed exactly as a five-spin problem, using LAOCOON II [S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964)]: $\tau_1 = 3.92$, $\tau_2 = \tau_3 = 7.69$, $\tau_4 = \tau_5 = 7.37$; $J_{12} = J_{13} = 8.41$, $J_{14} = J_{15} = -0.31$, $J_{23} = -13.03$, $J_{45} = -13.13$, $J_{25} = J_{34} = 10.54$, $J_{24} = J_{35} = 5.55$ c.p.s. (this laboratory).

(7) The structural assignments of VI, VII, and IX are made on the basis of the yields of each obtained, which correspond well to those predicted statistically for *trans* addition of bromine and *trans* elimination of hydrogen bromide and on the basis of conversion to II, whose structure is proved.

(8) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960); C. F. Wilcox, Jr., and J. G. Zajacek, *J. Org. Chem.*, **29**, 2209 (1964).

maximum σ-overlap of the p-orbitals. The HMO calculated ground-state energy lowering for IIa is equivalent to *ca.* 6 kcal./mole (β = 18 kcal./mole), whereas II, in a noncrown conformation, is expected to possess no D.E. Therefore, it is necessary to determine the conformation of II in order to gain information about any added stabilization due to π-electron delocalization.

Evidence favors a noncrown conformation. The melting point, −1.5°, seems low for II to have C_{3v} symmetry in comparison to I (m.p. 50°) and III (m.p. 34°). The ultraviolet spectrum of II showed only end absorption, unlike I, which has been proved to be in a crown conformation.[1c,1f] The dipole moment of VIII was found to be 0.6 D., showing that VIII is not in a crown conformation (a calculated dipole moment for VIII in a crown conformation is >3 D.). The magnitude of the vicinal coupling constants[6] for the ethano hydrogens of VIII (which is interconverting between equivalent conformers) strongly favors an *s-trans* arrangement. Molecular models show that IIc is less strained than IId and, in addition, that the bromines in VIII would cause no serious steric interactions in the various conformations considered.

Though the conformation of II is not proved, we conclude from these data that II is in a noncrown conformation and that its actual conformation is likely to be IIc. The conclusion that II is in a noncrown conformation, however, does not allow the inference that σ-overlap of the p-orbitals of a different cyclic π-electron system will be completely ineffective at lowering its ground-state energy. The conformer IIa, with C_{3v} symmetry, contains six pairs of eclipsed ethano hydrogens which alone could raise its energy by as much as 6 kcal./mole due to nonbonded interactions. Thus, any stabilization IIa may gain from π-electron delocalization is outweighed by its nonbonded interactions.

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Received March 19, 1965

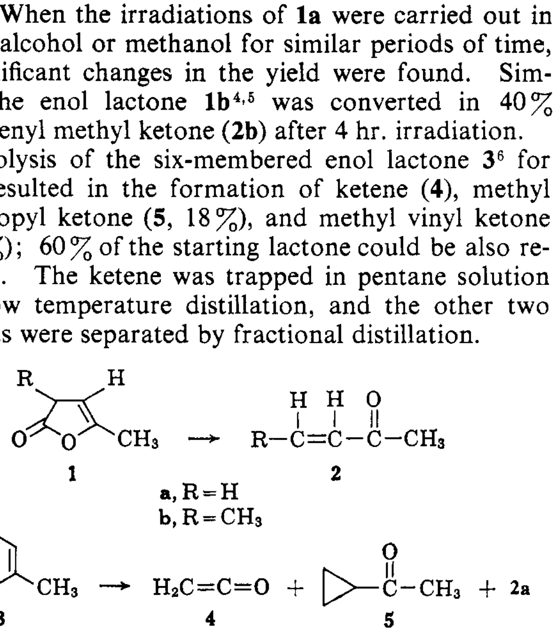
Irradiation of Enol Lactones

Sir:

We have recently reported on the irradiation of enol benzoates,[1] enol acetates,[2] and dienol acetates[3] by a low pressure mercury lamp. We wish now to report the extension of this study to include photochemistry of enol lactones by the same light source.

When angelica lactone (**1a**) was irradiated in pentane solution for 6 hr., it was converted in 30% yield to methyl vinyl ketone (**2a**), which could be obtained in pure form *via* direct distillation of the pentane solution. The residue consisted of unchanged starting lactone **1a**. No additional products could be detected by g.l.c. separation, and the n.m.r. spectrum of the total irradiated solution showed the signals due to **1a** and **2a** only. When the irradiations of **1a** were carried out in *t*-butyl alcohol or methanol for similar periods of time, no significant changes in the yield were found. Similarly the enol lactone **1b**[4,5] was converted in 40% to propenyl methyl ketone (**2b**) after 4 hr. irradiation.

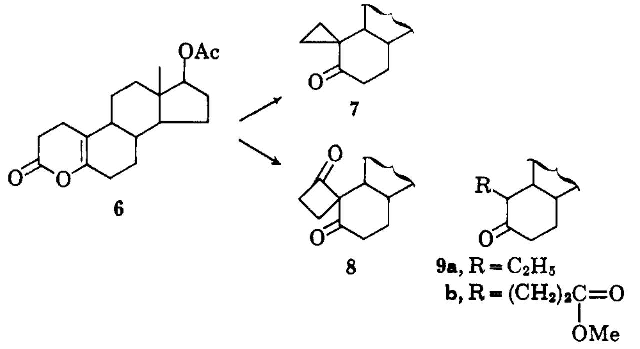
Photolysis of the six-membered enol lactone **3**[6] for 7 hr. resulted in the formation of ketene (**4**), methyl cyclopropyl ketone (**5**, 18%), and methyl vinyl ketone (**2a**, 7%); 60% of the starting lactone could be also recovered. The ketene was trapped in pentane solution by a low temperature distillation, and the other two products were separated by fractional distillation.

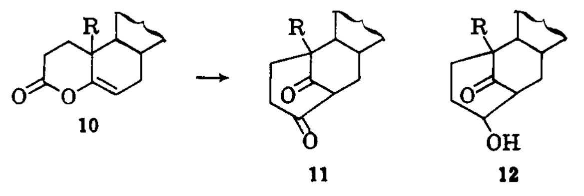


$$\text{R--CH=CH--}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{--CH}_3$$

Irradiation of analogous steroidal lactones **6**[7] for 20 min. resulted in *ca.* 50% conversion. The main product was the cyclopropyl ketone **7** (40%). In addition small amounts of cyclobutanone product **8** (3%) and a dimeric ketone $C_{34}H_{50}O_7$ (2%) were isolated. The structure of the cyclopropyl ketone **7** was deducted from its physical properties[5] and its reduction with zinc and acetic acid to the α-ethyl ketone **9a**, and that of cyclobutanone product **8**[5] from its ready methanolysis to the keto ester **9b**.

Irradiation of the exocyclic enol lactone **10a**[8] for 18 hr. resulted in the non-enolic diketone **11a** (15%; recovered starting lactone 50%). Its structure was established by a direct comparison with chromic acid





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[1] M. Gorodetsky and Y. Mazur, *Tetrahedron Letters*, 369 (1963).

[2] A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964).

[3] M. Gorodetsky and Y. Mazur, *ibid.*, **86**, 5213 (1964).

[4] Prepared from 2-methyl-4-ketopentanoic acid.

[5] Satisfactory elemental analyses and compatible ultraviolet, infrared, and n.m.r. spectra were obtained for all new compounds.

[6] D. Vorländer and A. Knötzsch, *Ann.*, **294**, 317 (1897).

[7] J. A. Hartman, A. J. Tomasewski, and A. S. Dreiding, *J. Am. Chem. Soc.*, **78**, 5662 (1956).

[8] G. I. Fujimoto, *ibid.*, **73**, 1856 (1951); H. J. Ringold and G. Rosenkrantz, *J. Org. Chem.*, **22**, 602 (1957).