

violet absorption bands^{3,11} at 230 and 292 $m\mu$ which are not seen in $B_{10}H_{10}^{-2}$ itself. In addition, the absence of B-H-B bands in the infrared spectrum of $B_{20}H_{18}^{-2}$ is now rationalized.

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(11) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

(12) Alfred P. Sloan Research Fellow.

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A 2,3-Diazacyclopropanone (Di-*t*-butyldiaziridinone)

Sir:

We wish to report the preparation of a new small-ring heterocycle, a diaziridinone (I, R = *t*-butyl) possessing a number of properties of special interest and of considerable potential as a synthetic intermediate.

Treatment of N,N'-di-*t*-butyl-N-chlorourea,¹ m.p. 30–31°, with potassium in pentane or with potassium *t*-butoxide in *t*-butyl alcohol² affords di-*t*-butyldiaziridinone (I, 40–80% yield), m.p. 0–1° (*Anal.* Found: C, 63.38; H, 10.74; N, 16.47), mol. wt. 178 (cryoscopic in cyclohexane), n.m.r. (in CCl_4), single peak at τ 8.80, infrared absorption in the carbonyl region (in CCl_4), maximum at 1880 and 1862 cm^{-1} with shoulders at 1926 and 1800 cm^{-1} . Chemical evidence in support of structure I³ is found in: (1) cleavage of the N–N bond by hydrogenation (palladium on carbon) with formation of N,N'-di-*t*-butylurea in 96% yield; (2) cleavage of the C–N bond by sodium borohydride with formation of N,N'-di-*t*-butyl-N-formylhydrazine (60% yield), m.p. 42–43°, n.m.r. (in CCl_4), τ 8.92 (singlet, 9 H's), 8.63 (singlet, 9 H's), 5.80 (broad, 1 H), and 1.43 (singlet, 1 H).

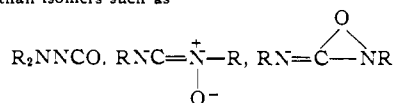
Compound I is reactive toward acids. Treatment of I with dry hydrogen chloride followed by water gives 2,3-di-*t*-butylcarbazyl chloride, II. Treatment of II with potassium *t*-butoxide in *t*-butyl alcohol yields a mixture of I (45%) and *t*-butyl 2,3-di-*t*-butylcarbazate (III, 25%).

Among the unusual properties of I are the high thermal stability (only slight decomposition in 2 hr. at 175°)

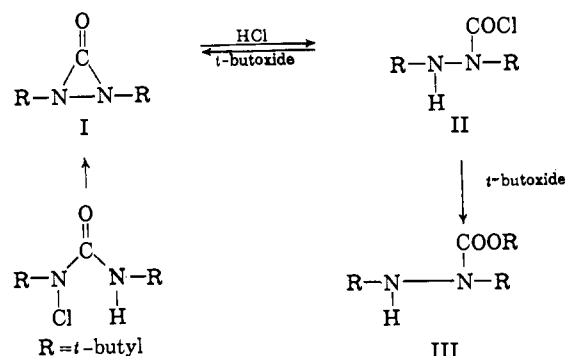
(1) Satisfactory combustion data and proof of structure have been obtained for new compounds.

(2) These methods are analogous to those used to prepare α -lactams: H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Am. Chem. Soc.*, **85**, 3303 (1963); J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 1356 (1964).

(3) The physical and chemical evidence appears in strong favor of structure I rather than isomers such as



X-Ray evidence on the structure and particularly on the interesting question of the location of the substituents relative to the plane of the ring will be forthcoming.



and the stability toward nucleophiles⁴ (50% conversion of I to III by potassium *t*-butoxide (0.3 *M*) in *t*-butyl alcohol in 16 hr. at reflux; no reaction of I with aniline in ether for 6 days at 25°).

The *t*-butyl carbazate, III, is readily cleaved by hydrogen chloride; the resulting N,N'-di-*t*-butylhydrazine may be directly oxidized to azo-*t*-butane (one of several procedures for the conversion of I to the azo compound). Thus the work described here represents a method for the formation from ureas of substituted⁵ hydrazines with like or unlike substituents and of symmetrical and unsymmetrical azo compounds.

A full account of the synthetic aspects and of the physical and chemical properties of compounds of type I will be reported at a later date.

(4) These properties are more reminiscent of the cyclopropanones [R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960); R. Breslow, J. Posner, and A. Krebs, *ibid.*, **85**, 234 (1963)] than of the α -lactams (ref. 2).

(5) E.g., *t*-alkyl; primary and secondary N,N'-disubstituted hydrazines are accessible from the corresponding azines.

(6) National Science Foundation Predoctoral Fellow, 1961–1964.

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Potassium Perxenate Nonahydrate¹

Sir:

Several salts of the unstable perxenic acid have been isolated and identified. Sodium perxenate^{2,3} exists in several crystalline forms, and the structures of $Na_4XeO_6 \cdot 8H_2O$ ^{4,5} and $Na_4XeO_6 \cdot 6H_2O$ ⁶ have been determined. Perxenate salts of barium^{7,8} and of calcium, lithium, and cesium⁸ have been prepared, but their structures are unknown. We have now prepared a potassium salt and characterized it as $K_4XeO_6 \cdot 9H_2O$ by determination of its crystal structure.

The solubility of potassium perxenate appears to be much greater than that of the sodium perxenates at a given concentration of OH^- . The disproportionation reaction of xenic acid in potassium hydroxide solution failed to give crystals under conditions analogous to those at which $Na_4XeO_6 \cdot 8H_2O$ was easily crystallized.

(1) Work done in part under the auspices of the U. S. Atomic Energy Commission.

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(3) S. Siegel and E. Gebert, ref. 2, p. 193.

(4) W. C. Hamilton, J. A. Ibers, and D. R. Mackenzie, *Science*, **141**, 532 (1963).

(5) J. A. Ibers, W. C. Hamilton, and D. R. Mackenzie, *Inorg. Chem.*, to be published.

(6) A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *Science*, **142**, 501 (1963).

(7) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(8) C. W. Koch and S. M. Williamson, unpublished work.

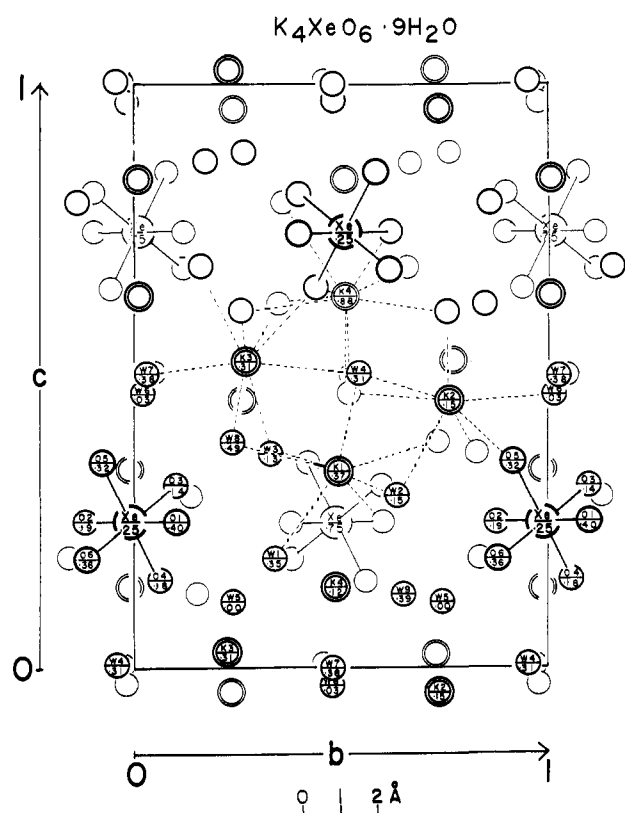


Fig. 1.—Crystal structure of $K_4XeO_6 \cdot 9H_2O$ viewed down the a -axis; the designation and x -coordinate are indicated on some of the atoms; broken lines connect potassium atoms to their neighbors.

Appelman and Malm⁷ have described other failures to obtain potassium perxenate. We obtained the potassium salt by the following procedure. A concentrated solution of reagent grade KOH was treated with a small amount of $KMnO_4(s)$ and was heated at 70° for 3 days, *i.e.*, until the purple color was no longer present. The solution (10.04 M) was decanted from the sediment and was used without further treatment. Prolonged exposure to the atmosphere was avoided, and all experiments were carried out in Pyrex ware. After thorough degassing, 200 μ l. of the base and 750 μ l. of 0.1082 M xenic acid, prepared by dissolution of $XeO_3(s)$, were mixed *in vacuo* at 0° . By gas evolution measurements similar to those previously described,⁹ it was determined that 26.06 μ moles of $Xe(VIII)$ was prepared. No crystals were obtained by cooling the solution to 0° . We removed 400 μ l. of H_2O *via* vacuum distillation and added 200 μ l. of the xenic acid. This increment of 21.64 μ moles of xenic acid produced only an additional 5.61 μ moles of $Xe(VIII)$. When this solution was cooled slowly to 5° , well-defined, colorless, transparent crystals appeared. After equilibrium at 5° was established, about three-fourths of the mother liquor was removed. The crystals in the remaining solution were stable and insoluble at room temperature. Before crystallization, the concentrations were $[Xe(VIII)] = 0.042$ and $[K^+] = 3.39 M$.

Crystals were studied by the same X-ray techniques which we used for sodium perxenate.⁶ The crystals of the potassium salt are considerably more stable in X-rays than $Na_4XeO_6 \cdot 6H_2O$, but less so than Na_4-

$XeO_6 \cdot 8H_2O$. Thus we were able to collect intensity data by direct counting with a single specimen (diameters 0.3 mm. or less), but the intensity scale had to be adjusted by a factor of 1.85 between the start and finish of the measurements. We used Mo $K\alpha$ radiation ($\lambda = 0.70926 \text{ \AA}$. for $K\alpha_1$). The measurements include all 1412 independent reflections permitted by the space group with 2θ less than 50° ; of these, we recorded 95 as zero. No correction was made for absorption or extinction.

The symmetry is orthorhombic, space group $Pbc2_1$ (C_{2v}^5), with $a = 9.049 \pm 0.004$, $b = 10.924 \pm 0.004$, $c = 15.606 \pm 0.006 \text{ \AA}$., $Z = 4$, $d_x = 2.35 \text{ g./ml}$. Each atom is in general positions $4(a)$: x, y, z ; $-x, -y, 1/2 + z$; $-x, 1/2 + y, z$; $x, 1/2 - y, 1/2 + z$.

By alternate Fourier and least-squares methods, we reduced the unreliability factor⁶ R to 0.063, with anisotropic thermal parameters for Xe and isotropic ones for K and O. A Fourier synthesis of ($F_{obsd} - F_{calcd}$) at this stage showed no peaks larger than 2.2 electrons per \AA^3 (near a potassium atom) and 1.4 electrons per \AA^3 (near an oxygen atom). Further refinement with potassium atoms assigned anisotropic thermal parameters reduced R to 0.058.

The composition is assigned as $K_4XeO_6 \cdot 9H_2O$ on the basis of the good agreement with the X-ray data.

Atomic coordinates are listed in Table I. The

TABLE I
ATOMIC COORDINATES AND THERMAL PARAMETERS^a

Atom	x	y	z	$B, \text{\AA}^2$
Xe	0.249	0.988	0.250	1.1 ^b
K(1)	0.628	0.987	0.339	2.1 ^b
K(2)	0.846	0.238	0.958	2.9 ^b
K(3)	0.307	0.227	0.026	3.2 ^b
K(4)	0.877	0.989	0.139	1.9 ^b
O(1)	0.403	0.101	0.251	2.4
O(2)	0.094	0.878	0.253	2.4
O(3)	0.138	0.096	0.316	2.0
O(4)	0.176	0.058	0.151	2.2
O(5)	0.323	0.918	0.351	1.6
O(6)	0.360	0.881	0.188	2.3
W(1) ^c	0.654	0.839	0.190	1.9
W(2)	0.850	0.136	0.297	1.9
W(3)	0.873	0.829	0.369	2.2
W(4)	0.692	0.046	0.506	3.0
W(5)	0.997	0.243	0.111	2.0
W(6)	0.967	0.980	0.972	2.7
W(7)	0.376	0.470	0.002	3.1
W(8)	0.493	0.262	0.886	3.1
W(9)	0.606	0.150	0.124	2.8

^a Standard deviations correspond to 0.02 \AA . or less for coordinates and 0.3 \AA^2 or less for B . ^b Value equivalent to average of anisotropic parameters. ^c W indicates oxygen atom of water molecule.

XeO_6^{4-} ion is in the shape of a regular octahedron within experimental accuracy, with average Xe-O distance $1.86 \pm 0.01 \text{ \AA}$., in excellent agreement with $1.864 \pm 0.012 \text{ \AA}$.⁵ and $1.84 \pm 0.02 \text{ \AA}$.⁶ found in the two sodium salts. The bond angles that would be 90° for a regular octahedron range from 88.8 to 91.2° ($\sigma = 0.7^\circ$). The four independent potassium atoms have, respectively, six, six, seven, and seven water molecules and two, one, one, and two oxygen atoms of perxenate as neighbors as indicated in Fig. 1 at distances ranging from 2.67 to 3.22 \AA . These neighbors are at the corners of very irregular polyhedra, and some other neighbors

(9) S. M. Williamson and C. W. Koch, ref. 2, p. 158.

are not much more distant. An intricate network of hydrogen bonds connects the entire structure.

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RECEIVED JUNE 26, 1964

Far-Infrared Studies of Intermolecular Forces. Dipole-Dipole Complexes

Sir:

Far-infrared spectra (between 150 and 50 cm^{-1}) of thirteen organic compounds have been obtained in this laboratory. A very broad absorption band in the range from 88 to less than 50 cm^{-1} has been observed in the spectra of those compounds which have a high dipole moment. These observations coupled with other evidence indicate that these broad, low frequency vibrations are vibrations involving the bond joining molecules together in dipole-dipole complexes. While considerable evidence has been reported previously¹⁻⁴ that highly polar organic molecules can undergo self-association or complexing, this evidence has usually been the result of classical, but indirect, studies of colligative properties or virial coefficients. The appearance of these low frequency bands gives a direct means of studying these complexing forces.

Observed frequencies for the compounds studied are listed in Table I along with the molecular weights and

TABLE I

VIBRATIONAL FREQUENCIES OF ORGANIC MOLECULES BETWEEN 50 AND 150 CM^{-1}

Compound	Molecular weight	Dipole moment, D. ⁵	Physical state	Frequencies, cm^{-1} a
Benzonitrile	103	3.9	Liquid	54 vbr
p-Chlorobenzonitrile	137	2.56	Liquid	113
Phthalonitrile	128	5.9 (calcd.)	Solid	72, 133
Terephthalonitrile	128	0	Solid	95, 154
Nitrobenzene	123	3.98	Liquid	<50 vbr
o-Dinitrobenzene	168	6.00	Solid	88, 113, 136
			Liquid	86 br
p-Dinitrobenzene	168	0	Solid	104, 125
Phenylacetylene	102	0.80	Liquid	
Acetonitrile	41	3.5	Liquid	87 vbr
			Vapor	65 vbr, w
Nitromethane	61	3.15	Liquid	60 vbr
Methyl thiocyanate	73	3.6	Liquid	68 vbr
Acetone	58	2.75	Liquid	<50 vbr
			Vapor	118
1-Bromobutane	136	1.97	Liquid	

^a v = very, br = broad, w = weak, italicized frequencies are those attributed to dipole-dipole interaction.

dipole moments⁵ of the compounds. These spectra were obtained with a Perkin-Elmer Model 301 double-beam spectrophotometer with a lower frequency limit of approximately 50 cm^{-1} . Since many of the observed bands have frequencies near 50 cm^{-1} and are extremely broad, it was difficult to observe the entire band and, therefore, to locate the center of the band accurately. For these bands, the frequency may be accurate only to $\pm 10 \text{ cm}^{-1}$.

- (1) J. S. Rowlinson, *Trans. Faraday Soc.*, **46**, 974 (1949).
- (2) J. D. Lambert, G. A. H. Roberts, J. S. Rowlinson, and V. J. Wilkinson, *Proc. Roy. Soc. (London)*, **A196**, 113 (1949).
- (3) E. L. Zhukova, *Opt. Spektroskopia*, **4**, 750 (1958).
- (4) A. M. Saum, *J. Polymer Sci.*, **42**, 57 (1960).
- (5) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. V, Longmans, Green and Co., New York, N. Y., 1954.

Low frequency absorptions such as those observed could also arise from internal molecular vibrations, lattice modes or other crystal effects, and/or torsional modes (e.g., methyl rotations). For the compounds listed in Table I, vibrational assignments have been made for benzonitrile,^{6,7} nitrobenzene,⁸ phenylacetylene,⁹ acetonitrile,¹⁰ acetone,¹¹ and nitromethane.¹² None of these assignments indicates an internal molecular vibration giving absorption below 130 cm^{-1} ; therefore, the observed bands below 88 cm^{-1} cannot be assigned to intramolecular vibrations.

Lattice modes can be eliminated in all the compounds examined as liquids, and the use of a polyethylene matrix to contain the sample¹³ minimizes possible crystallinity effects in the materials examined as solids.

Torsion modes can be eliminated from consideration in the cases of benzonitrile, where microwave studies¹⁴ have shown a linear CCN structure; nitrobenzene, where Raman data have been used to assign the nitro torsion at 130 cm^{-1} ; acetone, for which Fateley and Miller¹⁵ assign a weak band at 109 cm^{-1} to the methyl torsion; and methyl thiocyanate, for which Fateley and Miller¹⁶ assign a broad band at 131 cm^{-1} in both the liquid and solid to the methyl torsion. No methyl torsion would be expected in this region for acetonitrile due to the linear CCN structure.

The broad, low frequency band observed in liquid acetone is not seen in acetone vapor; instead we observe a much weaker, sharp band at 118 cm^{-1} (which is probably the very weak band reported Fateley and Miller¹⁵). This disappearance is consistent with dissociation of the dipole-dipole complexes, or clusters of complexes, in the vapor state. The broad band observed in liquid acetonitrile is still evident in the vapor spectrum, but is much less intense and apparently shifted somewhat to lower frequencies than in the liquid. This would be the expected behavior if the complex persisted in the vapor as has been postulated.^{1,2} Persistence of the complex in the vapor for acetonitrile, but not for acetone, is consistent with the relative magnitude of the dipole moments of these compounds.

We do not observe the broad absorption at 131 cm^{-1} reported by Fateley and Miller for liquid and solid methyl thiocyanate; instead our liquid spectrum shows a broad band centered near 68 cm^{-1} , while at 77°K. we find a band near 116 cm^{-1} . Such a frequency shift with decreasing temperature is consistent with the expected behavior of an intermolecular vibration, but is not consistent with a torsion mode. Coupling between the torsion and the dipole-dipole vibration may occur and would account, in part, for the extreme broadness of these bands.

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- (7) R. J. Jakobsen, Aeronautical Systems Division Technical Report 63-869, Sept., 1963.
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- (11) A. Hadni, *Ann. Phys.*, **10**, 874 (1955).
- (12) D. C. Smith, C. Y. Pan, and J. R. Nielson, *J. Chem. Phys.*, **18**, 706 (1952).
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- (15) W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **18**, 977 (1962).
- (16) W. G. Fateley and F. A. Miller, *ibid.*, **17**, 557 (1961).