

ogies,<sup>5</sup> and the geometry of the acetylenic portion resembles that of diadsorbed ethylene (C).



Here again, diadsorbed seems preferable to  $\pi$  complex,<sup>6</sup> but good evidence supports surface intermediates which resemble  $\pi$ -bonded diene and allyl.<sup>3,6</sup>

We suggest that bicyclononane- $d_{10}$  and - $d_{12}$  result from exchange of h,h and g,g. Adamantane (bicyclononane with carbon atoms 3 and 7 bridged by methylene) exchanges only one hydrogen atom per period of adsorption. Since all of its vicinal hydrogen atoms are rigidly staggered, this accords with predictions.<sup>2</sup> Accordingly, the atoms at carbon atom 9 in bicyclononane will not exchange in conjunction with others barring some transannular reaction. In exchange of 1,1,3,3-tetramethylcyclohexane on palladium,<sup>7</sup> there is a maximum at  $d_5$  in addition to one at  $d_3$  which results from alternation between A and B. Formation of bicyclononane- $d_{10}$  and - $d_{12}$  is consistent with the proposal<sup>7</sup> that  $d_{10}$  in cyclopentane and  $d_5$  in tetramethylcyclohexane result from alternation between  $\pi$ -bonded olefin and  $\pi$ -bonded allyl. This cannot exchange h' and g'.

These experiments were run in a flow apparatus with 5% palladium-on-alumina catalyst<sup>2</sup> previously reduced in hydrogen at 350°. The partial pressures were cyclopentane, 93 mm.; bicyclononane, 8 mm.; adamantane, 5 mm.; and deuterium to 1 atm.

**Acknowledgment.** This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 1579-C. We thank Dr. J. A. Marshall and Mr. C. J. V. Scanio for supplying us with the ethylene ketal of bicyclo[3.3.1]non-2-en-9-one and assistance in converting it to bicyclononane.

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## Volatile Rare Earth Chelates

Sir:

We have synthesized and characterized volatile chelates of 15 trivalent rare earths and have separated mixtures of the complexes by gas chromatography. The ligand employed in this study was 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane), hereafter abbreviated H(thd). The chelates are thermally stable, anhydrous, unsolvated compounds of the formula  $M(\text{thd})_3$ . Molecular weight measurements on the lanthanum, samarium, gadolinium, terbium, thulium, and ytterbium complexes indicate that the compounds are monomeric in benzene. Infrared measurements showing the absence of O-H stretching vibrations and the close agreement of elemental analyses have proved that the crystalline compounds are anhydrous.

The complexes readily undergo vacuum sublimation without apparent decomposition at temperatures between 100 and 200°. Differential thermal analyses and visual observations of melting behavior indicate that most of the complexes can be heated above 300° and then cooled and remelted at the original melting point. Thermal gravimetric analysis of  $\text{Er}(\text{thd})_3$  in a helium atmosphere showed that ca. 99% of the sample sublimed below 230°.

Efforts to synthesize the rare earth chelates by a previously reported method<sup>1</sup> produced only poor yields. It was reasoned that perhaps the low yields were caused by destructive air oxidation of the complexes in solution during the syntheses and subsequent recrystallizations. Oxidation of  $\text{Ni}(\text{thd})_2$  in solution has been found to occur readily.<sup>2</sup> A method in which air was excluded wherever possible was developed, and this has permitted the synthesis of the trivalent rare earth complexes in yields of 90–97%. The general method is illustrated by the preparation of  $\text{Tb}(\text{thd})_3$ . Sixty mmoles of H(thd) (Pierce Chemical Co.) was dissolved in 30 ml. of 95% ethanol in a thick-walled flask fitted with a stopcock connected to a vacuum system. NaOH (2.4 g.) dissolved in 50 ml. of 50% ethanol was added. The reactants were continuously stirred with a magnetic stirrer.  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (20 mmoles, prepared from 99.9%  $\text{Tb}_4\text{O}_7$ ) dissolved in 50 ml. of 50% ethanol was added. Immediately the flask was evacuated, sealed, and stirred for 2 hr. The volume of the solution was reduced by 50% by reduced pressure distillation, and 350 ml. of distilled water was added. The  $\text{Tb}(\text{thd})_3$  which separated was quickly vacuum filtered, dried, and sublimed at 180° *in vacuo*. The yield of sublimed product was 13.17 g. (92.9%). The sublimed crystals were recrystallized from *n*-hexane *in vacuo* and vacuum dried (m.p. 177–180°). The crystals of  $\text{Tb}(\text{thd})_3$  emit brilliant green fluorescence when irradiated at 3660 Å. with an ultraviolet lamp. Table I shows the melting points, elemental analyses, and, for the diamagnetic complexes, the proton n.m.r. spectra in carbon tetrachloride relative to internal tetramethylsilane.

One of the objectives of this study was to separate rare earth complexes by gas chromatography. All previous efforts have failed owing to the lack of volatility and the thermal instability of the other rare earth chelates examined.<sup>3,4</sup> Gas chromatographic experiments have shown that all of the thd chelates can be chromatographed without decomposition. Benzene solutions of each of the complexes were injected into the chromatographic column at 200°; the chromatogram of each complex showed a single peak well separated from the solvent peak. The crystalline complexes collected from the effluent carrier gas stream were shown to have been eluted without decomposition by comparison of melting points and ultraviolet and visible spectra with those of each complex before injection.

There appear to be appreciable and significant differences in the volatilities of the rare earth complexes

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(2) K. E. Johnson and G. S. Hammond, U. S. Atomic Energy Commission Report IS-215, 1959, 64 pp.

(3) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Ltd., Oxford, 1965, pp. 23, 36.

(4) J. C. Bailar, Jr., and D. H. Busch, "Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p. 42, and references cited therein.

Table I

Complex	M.p., °C.	Analysis						Proton n.m.r., p.p.m.	
		Theoretical <sup>a</sup>			Experimental <sup>a</sup>			CH <sub>3</sub>	CH
		C	H	Metal	C	H	Metal		
Sc(thd) <sub>3</sub>	152-155	66.64	9.66	7.56	66.64	9.40	6.97	1.12	5.78
Y(thd) <sub>3</sub>	169-172.5	62.06	9.00	13.92	61.84	9.06	13.38	1.12	5.74
La(thd) <sub>3</sub>	238-248 <sup>b</sup>	57.55	8.34	20.17	57.42	8.43	20.42	1.08	5.68
Pr(thd) <sub>3</sub>	222-224 <sup>b</sup>	57.38	8.32	20.40	57.34	8.26	20.43		
Nd(thd) <sub>3</sub>	215-218 <sup>b</sup>	57.11	8.28	20.78	57.02	8.34	20.78		
Sm(thd) <sub>3</sub>	195.5-198.5	56.61	8.21	21.47	56.47	8.15	21.49		
Eu(thd) <sub>3</sub>	187-189	56.48	8.19	21.65	56.37	8.26	21.83		
Gd(thd) <sub>3</sub>	182-184	56.06	8.13	22.24	56.22	8.17	22.11		
Tb(thd) <sub>3</sub>	177-180	55.93	8.11	22.42	56.04	8.18	22.23		
Dy(thd) <sub>3</sub>	180-183.5	55.64	8.07	22.81	55.77	8.18	22.82		
Ho(thd) <sub>3</sub>	180-182.5	55.46	8.04	23.08	55.40	7.97	23.29		
Er(thd) <sub>3</sub>	179-181	55.28	8.01	23.33	55.25	7.96	23.17		
Tm(thd) <sub>3</sub>	171.5-173.5	55.15	7.99	23.50	54.92	7.92	23.46		
Yb(thd) <sub>3</sub>	166-169	54.83	7.95	23.94	54.79	8.10	23.81		
Lu(thd) <sub>3</sub>	172-174	54.69	7.93	24.14	54.61	7.95	23.96	1.16	5.79

<sup>a</sup> Elemental analysis performed by Galbraith Laboratories, Knoxville, Tenn. <sup>b</sup> Melting point taken in a sealed, evacuated capillary tube.

as indicated by sublimation and gas chromatographic retention data. For example, Lu(thd)<sub>3</sub>, Yb(thd)<sub>3</sub>, and Tm(thd)<sub>3</sub> sublime at temperatures about 100° lower than those required for La(thd)<sub>3</sub>, Pr(thd)<sub>3</sub>, and Nd(thd)<sub>3</sub>. The volatility differences have made it possible to separate rare earth complexes by fractional sublimation. A thermal gradient fractional sublimation apparatus (a modified version of the device described by Berg and Hartlage<sup>5</sup>) was constructed. The device was operated

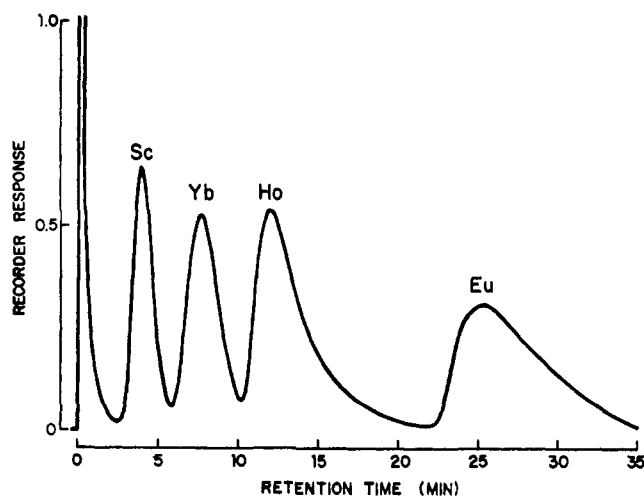


Figure 1. Gas chromatographic separation of volatile rare earth thd complexes: benzene solution (8  $\mu$ l.) separated on a Teflon column (15 cm. long  $\times$  5 mm. i.d.) containing 2% Apiezon H on Gas-Pack F (60-80 mesh); instrument, F and M Model 810; column temperature, 157°; injection port temperature, 228°; thermal conductivity cell temperature, 232°; helium flow rate, 100 cc./min.

at atmospheric pressure with helium as a carrier. An equimolar mixture of Tb(thd)<sub>3</sub> and La(thd)<sub>3</sub> was introduced into the hottest zone of the tube. The thermal gradient along the tube ranged from 187° in the hottest zone to 60° at the cold end. The more volatile Tb(thd)<sub>3</sub> moved much further into the cooler zone than did the lanthanum complex. The crystals that deposited in the temperature zone from 72 to 141° melted at 178-180° and emitted brilliant green fluorescence characteristic of the terbium complex, while the crystals found in the

(5) E. W. Berg and F. R. Hartlage, *Anal. Chim. Acta*, **33**, 173 (1965).

zone from 141 to 187° exhibited no trace of fluorescence.

Figure 1 shows a gas chromatographic separation of a benzene solution of a mixture of thd complexes. A glass-liner insert was used in the injection port throughout the study; no residue indicative of decomposition was found when the insert was examined after chromatographing the complexes. Fractions of each of the four complexes were collected and examined to verify

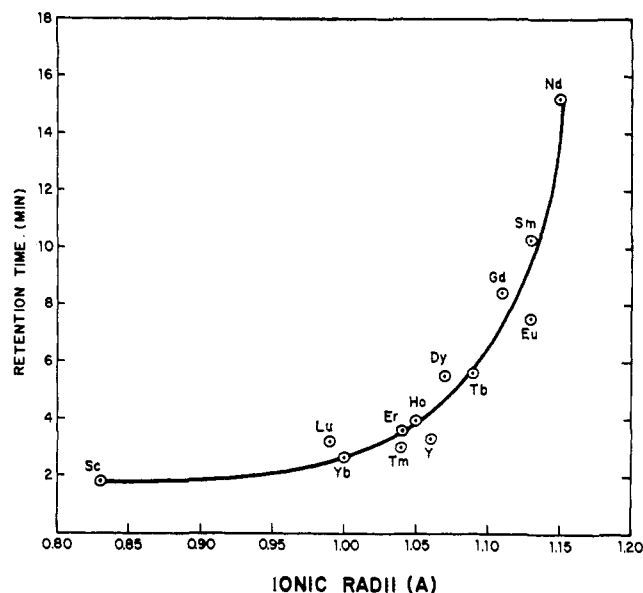


Figure 2. Retention times for rare earth thd complexes as a function of ionic radii: column, Teflon (15 cm.  $\times$  5 mm. i.d.) containing 10% Apiezon N on Gas-Pack F (60-80 mesh); column temperature, 185°; injection port temperature, 228°; detector temperature, 232°; helium flow rate, 150 cc./min. At this column temperature Pr(thd)<sub>3</sub> and La(thd)<sub>3</sub> were eluted after several hours.

that the compounds were eluted without decomposition and that the peak assignments are correct. Further studies of the gas chromatographic and fractional sublimation techniques are being made in an effort to improve the separations and extend the techniques to more complex and difficultly separable mixtures.

Examination of the gas chromatographic retention behavior of the complexes reveals an interesting relationship depicted in Figure 2. The retention behavior

shows clearly the effects of the lanthanide contraction. The volatility of the complexes appears to decrease<sup>6</sup> as the size of the metal ion (as indicated by the empirical ionic radii of the trivalent ions<sup>7</sup>) increases. This can be explained if it is assumed that in going from the lighter, larger, less volatile lanthanides to the smaller members local dipoles that act to decrease volatility either become smaller or else are more effectively shielded from near neighbors as the outer ligand shell becomes more compact. It should be noted that the retention times cannot be correlated with mass. The yttrium complex has about the same retention time as that of erbium even though the atomic weight of yttrium is only about one-half that of erbium.

Work in this laboratory now in progress is directed to the synthesis of derivatives of H(thd), particularly of the type in which fluorocarbon moieties are incorporated, in hopes of obtaining complexes that are even more volatile. Spectral, magnetic susceptibility, and single crystal X-ray data are also being studied<sup>8</sup> to further characterize these unusually volatile complexes.

**Acknowledgment.** This research was supported in part by the ARL In-House Independent Laboratory Research Funds, Office of Aerospace Research, U. S. Air Force.

(6) That the increase in retention times reflects decreasing volatility is inferred from the fractional sublimation data.

(7) V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, 8, 69 (1926); *Ber.*, 60, 1263 (1927).

(8) E. A. Boudreaux and L. M. Trefonas, private communication, Aug. 1965.

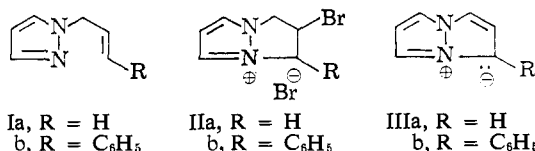
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#### 4,8-Diazapentalene<sup>1</sup>

Sir:

In two earlier publications<sup>2</sup> we reported the synthesis of stable 1-benzoyl-2-phenyl derivatives of the 4,8-diazapentalene<sup>3</sup> system (IIIa). We now report p.m.r.



evidence for the existence of the parent 4,8-diazapentalene (IIIa) and its 1-phenyl derivative (IIIb).

1-Allylpyrazole<sup>4</sup> was treated with bromine in 48% hydrobromic acid. The crude dibromide that formed underwent cyclization in boiling acetone to IIa, m.p. 156.5–159° (p.m.r.: doublet,  $\tau$  1.33; triplet, 2.98; multiplet, 4.38; multiplet, 4.96; areas 2:1:1:4).<sup>5</sup> The bromo compound, IIa, was then dissolved in deuteriodimethyl sulfoxide in a p.m.r. tube and treated with an excess of lithium hydride. A nitrogen atmosphere was provided and the tube was sealed. The

(1) Presented at the Heterocyclic Chemistry Conference, Bozeman, Mont., Aug. 12, 1965.

(2) (a) T. W. G. Solomons and F. W. Fowler, *Chem. Ind. (London)*, 1462 (1963); (b) T. W. G. Solomons, F. W. Fowler, and J. Calderazzo, *J. Am. Chem. Soc.*, 87, 528 (1965).

(3) Pyrazolo[1,2-*a*]pyrazole.

(4) I. L. Finar and K. Utting, *J. Chem. Soc.*, 5272 (1960).

(5) Satisfactory analytical and p.m.r. data have been obtained for all new compounds reported. Wherever possible picrates and tetraphenylboron derivatives were also prepared and analyzed.

p.m.r. spectrum showed the characteristic A<sub>2</sub>X spectrum expected for the 4,8-diazapentalene. The spectrum consisted of a doublet at  $\tau$  2.95 and a triplet at  $\tau$  3.52 with  $J = 2.5$  c.p.s. The ratio of intensities was 2:1.<sup>6</sup> The aliphatic protons present in IIa were all absent, and the only other peaks present were assigned to LiOH<sup>7</sup> and the solvent. It is interesting to note the shift in positions of the A<sub>2</sub>X protons of the pyrazolium ring in IIa as it is transformed to IIIa. The 1 and 3 protons of the pyrazolium compound are shifted upfield by 96 c.p.s., while the 2 proton is shifted upfield by only 32 c.p.s. This is consistent with the change from a ring bearing a positive charge (IIa) to a neutral system (IIIa) in which resonance structures place a negative charge on the 1 and 3 positions.

Cinnamylpyrazole (Ib),<sup>5</sup> b.p. 101° (0.025 mm.), was converted to the salt IIb,<sup>5</sup> m.p. 164–166°, by bromination and cyclization. Dehydrobromination of IIb with lithium hydride in deuteriodimethyl sulfoxide produced what we believe to be 1-phenyl-4,8-diazapentalene (IIIb). The p.m.r. spectrum showed a complex multiplet in the region  $\tau$  2.33–3.36. All of the peaks due to the aliphatic protons in IIb disappeared during the conversion.

When exposed to air, a solution of the 4,8-diazapentalene rapidly oxidized to a dark insoluble substance. This oxidation seems to be much slower in dimethyl sulfoxide than in other solvents which were tried.

4,8-Diazapentalene formed an orange crystalline picrate,<sup>5</sup> m.p. 140–141°. Attempts to form an adduct with methyl propiolate or dimethyl acetylenedicarboxylate have so far been unsuccessful. Benzoylation has also been attempted and resulted in a very dark solid which melts above 360°.

The visible-ultraviolet spectra of IIIa and IIIb were measured in 95% ethanol.<sup>8</sup> Maxima were found at 257 m $\mu$  (log  $\epsilon$  3.7) and 465 m $\mu$  (log  $\epsilon$  3.5) for IIIa and 254 m $\mu$  (log  $\epsilon$  4.1) and 480 m $\mu$  (log  $\epsilon$  3.5) for IIIb.

**Acknowledgment.** The authors are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for support of this work.

(6) It should be noted that the 4,8-diazapentalene absorbs at lower fields than the pentalene dianion, and the relative positions of the doublet and triplet are reversed. Cf. T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, 86, 249 (1964).

(7) The salt IIa was partially hydrated.

(8) Weighed amounts of IIa and IIb were placed in nitrogen-flushed volumetric flasks. Excess lithium hydride and a small amount of dimethyl sulfoxide were added. When the reaction was completed the mixture was diluted with 95% ethanol and the spectra were determined.

(9) American Chemical Society Petroleum Research Fund Undergraduate Scholar, 1964–1965; National Science Foundation Undergraduate Research Participant, 1965.

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#### On the Inertia of Aqueous Phosphite Ion to Oxidation

Sir:

Recent work on the oxidation of arsenite<sup>1</sup> and of sulfite<sup>2</sup> by HCrO<sub>4</sub><sup>-</sup> in aqueous solution containing

(1) J. G. Mason and A. D. Kowalik, *Inorg. Chem.*, 3, 1248 (1964).

(2) G. P. Haight, Jr., E. Perchonock, P. Emmenegger, and G. Gordon, *J. Am. Chem. Soc.*, 87, 3835 (1965).