tra are particularly weak and are comparable to the spectra of the $LnCl_6^{3-}$ ions.[6] The results are consistent with an essentially octahedral arrangement of ligands in $Ln(NCS)_6^{3-}$. The solution spectra of the complexes of the heavier lanthanides are also consistent with this hypothesis. The spectra of the complexes of the lighter lanthanides, however, indicate that the symmetry is less than octahedral in these solutions.

Crystals of the erbium(III) salt contain four $\{(C_4H_9)_4N\}_3Er(NCS)_6$ species in an A-centered triclinic cell of dimensions[7] $a = 22.63 \pm 0.03$ Å, $b = 16.73 \pm 0.02$ Å, $c = 18.82 \pm 0.02$ Å, $\alpha = 87.97 \pm 0.02°$, $\beta = 89.08 \pm 0.03°$, $\gamma = 92.47 \pm 0.03°$. The absence of any observable piezoelectric effect and the successful structure determination indicate the space group to be $A\bar{1}$, necessitating the placement of 70 atoms in the asymmetric unit. X-Ray intensity data were measured to a limit of $\theta_{Mo} < 20°$ *via* the moving-crystal–moving-counter technique on a Picker four-circle diffractometer. Placement of the erbium from a Patterson synthesis followed by solution of Fourier syntheses phased on the heavy atoms led to the crystalline arrangement. A least-squares refinement with isotropic thermal parameters was carried out in which only correlations between parameters of atoms within a given hexaisothiocyanatoerbium(III) or tetrabutylammonium ion were considered. The conventional discrepancy factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for the 3406 data thus far used in the refinement has been reduced from 0.48, for the erbium contribution only, to 0.12 at present. A difference map confirms the correctness of the structure.

The erbium(III) is N-bonded to six thiocyanates in an octahedral arrangement of essentially O_h-m3m symmetry. At the present stage of refinement we do not detect chemically significant deviations from this symmetry; we shall thus use average values for the bond lengths and angles in the following discussion and indicate the average value of an *individual* standard deviation in parentheses. The six Er–N bond lengths average to 2.34 (2) Å, somewhat shorter than that predicted by summing the atomic radii of erbium and nitrogen.[8] The Er–N–C–S groups are approximately linear with Er–N–C and N–C–S angles, 174 (2) and 176 (3)°, respectively. The nearness of the Er–N–C angle to 180° has been used as a criterion for the dominance of the $M—N^+\equiv C—S^-$ resonance structure in metal isothiocyanates.[9,10] Consistent with this hypothesis is the shortness of the N–C bond (1.10 (3) Å). The S–C bond length of 1.61 (3) Å is consistent with others reported[10] although shorter than that predicted by the resonance form above.[9]

Crystals of the tetra-*n*-butylammonium hexaisothiocyanatolanthanide(III) salts provide excellent examples of an ordered, magnetically dilute lanthanide ion of idealized O_h local symmetry; owing to the presence of the bulky $(C_4H_9)_4N$ cations, the closest Er–Er interaction is 11.7 Å. Preliminary magnetic studies[11] show the magnetic moment of the erbium complex to be 9.48 BM, in good agreement with the predicted value for an octahedral complex.[12]

Examination of the nonbonded distances between the alkylammonium groups and the thiocyanates indicate only normal van der Waals interactions and very little penetration of the butyl groups into the sphere of influence defined by the sulfurs. We thus do not attribute the surprising stability of these hexacoordinated lanthanides to a stabilizing influence of the cations in the crystal structure.

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[6] J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, **70**, 2845 (1966).

[7] This corresponds to a primitive cell of dimensions: $a = 22.63$ Å, $b = 12.39$ Å, $c = 12.83$ Å, $\alpha = 96.52°$, $\beta = 91.13°$, $\gamma = 92.35°$.

[8] J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

[9] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 273–274.

[10] For tabulations of data on metal isothiocyanates, see J. R. Knox and K. Eriks, *Inorg. Chem.*, **7**, 84 (1968); and A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).

[11] R. L. Lintvedt, private communication. Temperature-dependent single-crystal magnetic studies are in progress on these compounds.

[12] W. G. Penney and R. Schlapp, *Phys. Rev.*, **41**, 194 (1932); J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

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Received May 20, 1968

A Novel Route to α-Aminoalkylphosphonic Acids and Dialkyl α-Aminoalkylphosphonate Hydrochlorides

Sir:

It was recently reported that dialkyl aroylphosphonates could be converted to the corresponding oximes in high yield.[1] Reduction of the oximes by Al–Hg in ethanol–water proved highly successful for the synthesis of dialkyl α-aminoarylmethylphosphonates. Unfortunately, the method was inferior for the preparation of dialkyl α-aminoalkylphosphonate hydrochlorides or α-aminoalkylphosphonic acids, the phosphorus analogs of α-aminoalkylcarboxylic acids. Although a few methods[2] have been published for the synthesis of α-aminoalkylphosphonic acids, the present approach avoids the previous intrinsic limitations of low yields, long routes, and difficultly accessible starting materials. Diethyl acylphosphonates **1** are readily available[3] and are converted by methoxylamine hydrochloride to the O-methylated oximes **2** as shown in route A. Reduction of **2** in THF with diborane gave diethyl α-aminoalkylphosphonates which were dissolved in ether and converted by treatment with hydrogen chloride to the hydrochloride salts **3**.[4] Acid hydrolysis of **3**, after removal of the water at aspirator pressure, gives semisolids. Solution of the semisolids in a mini-

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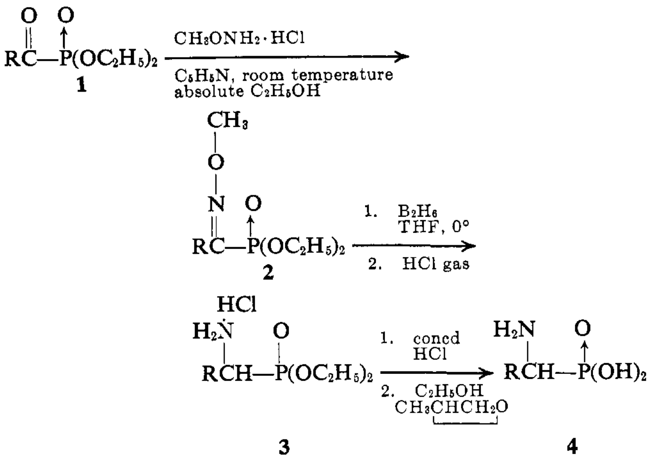
[1] K. D. Berlin, R. T. Claunch, and E. T. Gaudy, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P136.

[2] (a) J. R. Chambers and A. F. Isbell, *J. Org. Chem.*, **29**, 832 (1964); (b) M. I. Kabachnik and T. Ya. Medved, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 868 (1953); *Chem. Abstr.*, **49**, 840 (1955); (c) M. E. Chalmers and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 5278 (1953); (d) M. I. Kabachnik and T. Ya. Medved, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 314 (1954); *Chem. Abstr.*, **48**, 10541 (1954); (e) M. I. Kabachnik and T. Ya. Medved, *Dokl. Akad. Nauk SSSR*, **83**, 689 (1952); (f) G. M. Kosolopaff, *J. Am. Chem. Soc.*, **70**, 1283 (1948); (g) G. M. Kosolopoff, *ibid.*, **69**, 2112 (1947).

[3] K. D. Berlin, D. M. Hellwege, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1265 (1965); previous work is referenced in this paper.

[4] The technique used here was similar to that reported for reduction of O-methyl oximes of simple ketones; see H. Feuer, B. F. Vinvent, Jr., and R. S. Bartlett, *ibid.*, **30**, 2877 (1965). In our work, diborane was passed directly into a solution of **2** in THF.

Route A



mum of alcohol and treatment of the solution with propylene oxide result in the precipitation of **4**. Table I contains pertinent data for the conversion of **1** → **2** → **3** → **4**. It appears that good confirmation of structure for most of the α-aminoalkylphosphonic acids in the literature is meager or totally lacking.

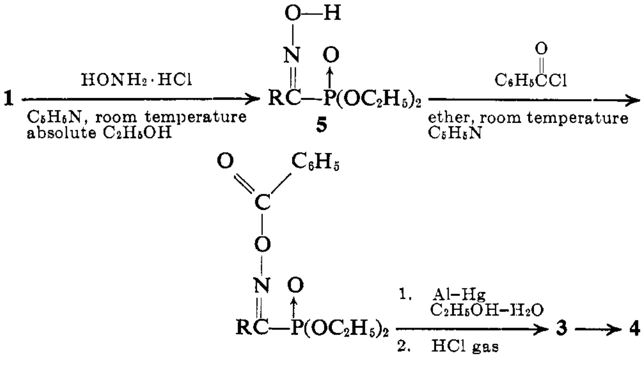
Table I. Conversion of $R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2$ (**1**) → **2** → **3** → **4**

R	**2** Bp, °C (mm)	**3** Mp, °C	**4** Mp, °C	Yields, % 1 → 2	2 → 3	3 → 4
CH_3	80 (1.2)	Liquid[a]	278	83	56	96
CH_3CH_2	85 (1.0)	Liquid[a]	271	80	55	96
$CH_3(CH_2)_2$	80 (0.5)	135	276	84	57	96
$CH_3(CH_2)_3$	100 (1.3)	122	277	80	56	95
$(CH_3)_2CH$	76 (0.5)	116	274	80	57	96
$(CH_3)_2CHCH_2$	98 (0.5)	134	279	80	56	95
$CH_3CH_2C(CH_3)H$	75 (0.15)	129	274	80	58	95

[a] These amine hydrochlorides did not crystallize upon standing at 0° for 1 week. They were converted to the corresponding acid without further purification.

Starting from **1**, each member of **3** and **4** could be synthesized *via* the alternative route B, but the overall yields of **3** and **4** were always lower by 10–20%.

Route B



Mixture melting point determinations, and ir and nmr spectra confirmed the identity of each compound in **3** and **4**. Table II contains ^{31}P nmr data not previously recorded for some members of **3** and **4**. The crude oximes **5** and crude esters **6** were used in the scheme without purification.

Table II. ^{31}P Data for α-Aminoalkyl- and α-Aminoarylphosphonic Acids and the Hydrochloride Salts of the Diethyl Esters

$\overset{NH_3^+Cl^-}{\overset{\vert}{RCHPO_3Et_2}}$, R =	Chemical shift, ppm[a]	$\overset{NH_2}{\overset{\vert}{RCHPO_3H_2}}$, R =	Chemical shift, ppm[b]
$(CH_3)_2CH$	−21.26	CH_3	−17.62
$CH_3CH_2C(CH_3)H$	−21.34	$(CH_3)_2CH$	−16.36
C_6H_5	−17.5; $J = 8.4$ cps	$(CH_3)_2CHCH_2$	−18.13
p-$CH_3OC_6H_4$	−18.2; $J = 8.1$ cps	p-$CH_3OC_6H_4$	−13.33
p-$(CH_3)_3CC_6H_4$	−17.35; $J = 8.4$ cps		

[a] Measured in H_2O from the external standard of 85% H_3PO_4.
[b] These compounds were dissolved in 85% H_3PO_4, and the spectrum was obtained quickly. Only the chemical shifts could be measured, since the viscous solutions were obtained and precluded enough resolution to see splitting patterns. Dilution with H_2O caused precipitation. Unfortunately, the acids were not sufficiently soluble in other solvents to obtain ^{31}P spectra or chemical shifts.

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(5) We gratefully acknowledge support from the Public Health Service, Grant No. GM 10367-06.

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Received May 15, 1968

The Tri-*t*-butylcyclopropenyl Cation

Sir:

We wish to report the first synthesis of the tri-*t*-butylcyclopropenyl cation *via* di-*t*-butylcyclopropenone. Reaction of α,α′-dibromodineopentyl ketone with potassium *t*-butoxide in tetrahydrofuran afforded, after sublimation of the crude product at reduced pressure, cyclopropenone I[1–3] in 35–40% yield, mp 61.5–62°. *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.45; H, 10.82. With the exception of the parent ion peak at *m/e* 166 the mass spectrum is very similar to that of di-*t*-butylacetylene. The infrared spectrum (CCl_4 solution) shows bands at 2980 (s), 2945 (m), 2920 (m), 2880 (m), 1875 (m), 1855 (s), 1820 (s), 1640 (s), 1485 (m), 1465 (m), and 1375 cm^{-1} (m). In addition to strong end absorption, I (in 95% EtOH) exhibited the characteristic n → π* absorption of cyclopropenones in the ultraviolet at 260 mμ (ε 45.5).[1b,4,5]

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(1) The method employed was essentially that of Breslow: (a) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965); (b) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).

(2) Professor F. D. Greene has kindly informed us that he has also prepared di-*t*-butylcyclopropenone by the same pathway.

(3) Compound I can also be prepared in very low yield by the reaction of di-*t*-butylacetylene with sodium trichloroacetate in refluxing dimethoxyethane followed by aqueous hydrolysis.