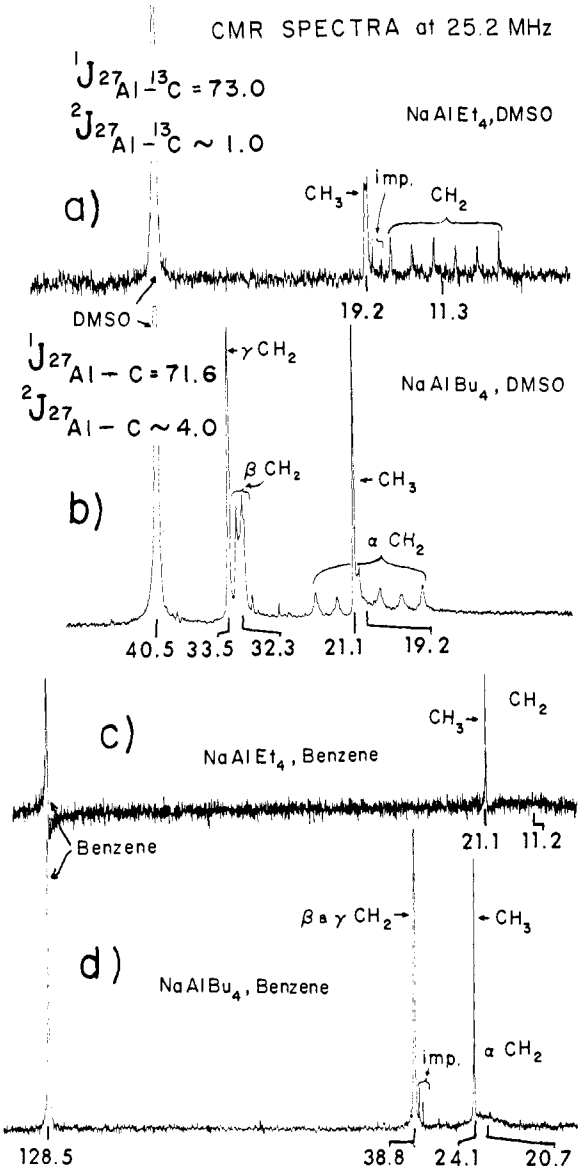

Figure 1. Proton-decoupled 25.2-MHz Fourier-transformed cmr spectra of $NaAlEt_4$ and $NaAlBu_4$ in DMSO and in benzene; chemical shifts are expressed in ppm downfield from Me_4Si.

phenomenon, no such interaction involving the aluminum-27 nucleus has been previously reported. The carbon atom one position removed from the aluminum atom also couples with this nucleus, but the magnitude of the spin interaction is severely attenuated with distance.

Secondly, the individual resonances of the carbon-13 nuclei adjacent to the aluminum atom are completely visible and uncomplicated by spin interactions with other carbon atoms. This is the case even in the spectrum of $NaAlBu_4$. Consequently, systematic alterations in these signals can be generated, observed, and, presumably, interpreted.

Thirdly, the α-carbon resonances in the cmr spectrum of solutions of the two compounds in benzene are observed as extremely broad signals that appear to be on the verge of coalescing into singlets. Similar coalescence phenomena in the pmr spectra of alkali metal tetramethylaluminate salts[3b,c] and, especially, of $NaAlEt_4$[3e] have been correlated successfully with degradations of symmetry in the electric field surrounding the tetrahedrally substituted quadrupolar aluminum atom. In as much as the present data indicate species in DMSO in which the aluminum resides in a stable, symmetrical electric environment, and ionic aggregates in benzene, in which proximal ions generate an electric field gradient within the aggregate, by analogy it appears that the same general phenomena are influencing pmr and cmr spectral line shapes. Thus, cmr spectroscopy does indeed offer a means of extending the direct[6] nmr approach to include a broader range of solutes (most imminently $NaAlBu_4$) and solvents, whose overlapping proton resonances would interfere with pmr studies. The influences of temperature and concentration upon the spectrum, as well as solvent effects upon chemical shifts, are in the process of being explored.

The preparation[7] of $NaAlBu_4$ and $NaAlEt_4$ and the purification[1c] of the solvents are recorded elsewhere. Fourier-transformed cmr spectra were recorded at 25.2 MHz with a Varian XL-100 spectrometer at a probe temperature of 70° in 8-mm sample tubes. Concentrations were 0.69 *m* except for $NaAlEt_4$ in benzene, which was determined as a saturated (~0.3 *m*) solution at the probe temperature.

Acknowledgment. We wish to express our appreciation for support of this work by National Science Foundation Grant No. GP-11427 and to the Spectroscopy Applications Laboratory of Varian Associates for the use of their XL-100 spectrometer.

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Deoxyoligonucleotide Synthesis Using a New Phosphate Protecting Group

Sir:

A number of groups have been proposed for the protection of the phosphate group in mononucleotides so as to synthesize di-, tri-, and higher oligodeoxynucleotides carrying 5′-phosphate end groups.[1] Some of the protecting groups are β-cyanoethyl,[2] trichloroethyl,[3] aromatic phosphoramidates,[4,5] substituted phosphorothioate,[6] *N*-(*p*-methoxyphenyl)carbamoylethyl,[7] and 4-hydroxy-2-sulfolene.[8] These groups vary greatly in the ease and efficiency with which they afford the

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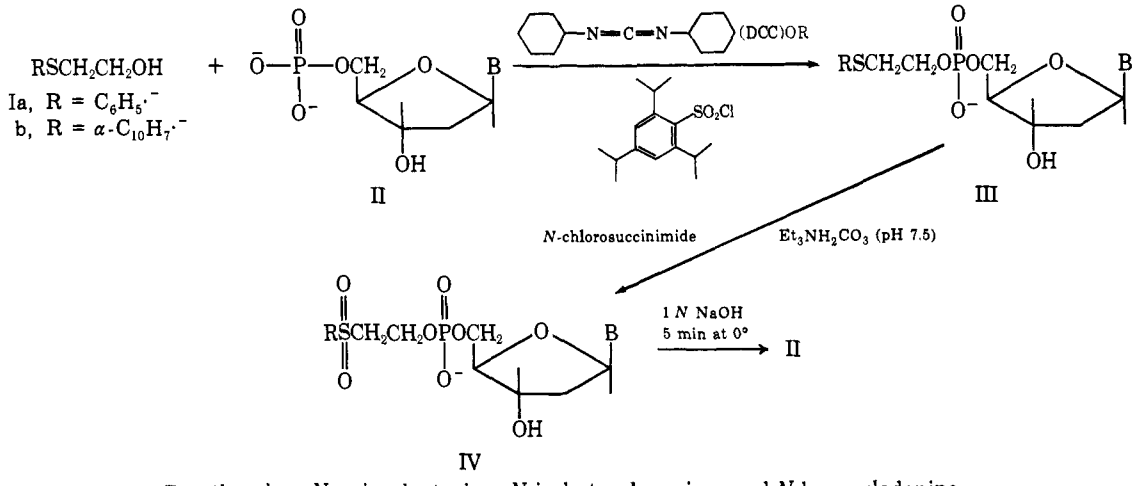
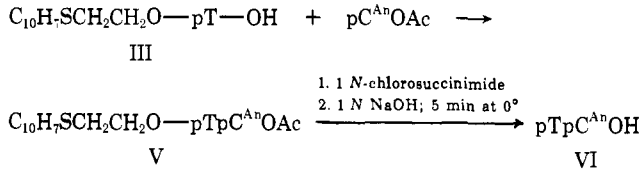


B = thymine, *N*-anisoylcytosine, *N*-isobutyrylguanine, and *N*-benzoyladenine

protected nucleotides and in the conditions required for their removal. In this communication, we report on the use of S-substituted mercaptoethanols (I) as a new class of phosphate protecting groups. Nucleotides can be derivatized easily in high yields using these protecting groups and their removal is achieved safely and quantitatively under very mild conditions.

The phosphate-protected derivatives (III) of all the four mononucleotides were prepared and isolated in quantitative yields. In a typical experiment Ib (5 mmol) was condensed with II (B = thymine, 1 mmol) in anhydrous pyridine, using either dicyclohexylcarbodiimide (DCC) (10 mmol) for 12 hr at room temperature or triisopropylbenzenesulfonyl chloride (TPS) (4 mmol) for 3 hr at room temperature. The reaction mixture was extracted with ether to remove unreacted Ib followed by a methylene dichloride–*n*-butyl alcohol (7:3, v/v) mixture which extracted III (R = $C_{10}H_7$; B = thymine) in quantitative yield. The protecting group was removed by oxidation of the sulfide ester (III, R = C_6H_5, $C_{10}H_7$) with *N*-chlorosuccinimide in $Et_3NH_2CO_3$ or phosphate buffer (pH 7.5) for 10 min at 0° followed by 1 *N* NaOH treatment for 5 min at 0°. Under these conditions, the appropriately protected mononucleotides showed no loss of the N-protecting groups or any other side reactions. Narang, *et al.*,[9] have recently described the use of Ia in a similar procedure, but the conditions used for the removal of the phosphate-protecting group are relatively severe. These authors have oxidized the sulfide ester to the sulfoxide with $NaIO_4$ and then subjected the sulfoxide ester to 2 *N* NaOH for 30 min at room temperature for removal. These conditions for the alkaline treatment are required for removal of the sulfoxide ester evidently due to the slow β elimination.



The protected mononucleotides III (R = C_6H_5 or $C_{10}H_7$) have been used for the synthesis of dinucleotides. In a typical experiment, III (0.5 mmol; R = $C_{10}H_7$; B = thymine) was condensed in pyridine with N^6-anisoyl-3′-acetyldeoxycytidine 5′-phosphate (pC^{An}OAc) (0.75 mmol) in the presence of triisopropylbenzenesulfonyl chloride (1.5 mmol) for 2 hr at room temperature. The reaction mixture was subjected to tritylcellulose chromatography.[1,10] The column was first washed with 0.05 *M* $Et_3NH_2CO_3$ containing 10% ethyl alcohol to remove pC^{An}OAc and its symmetrical pyrophosphate. Elution with 0.05 *M* $Et_3NH_2CO_3$ in 60% ethyl alcohol eluted a mixture of III and V which was further extracted with methylene dichloride–*n*-butyl alchol (7:3, v/v) to remove unreacted III. The dinucleotide V was isolated in 85% yield. Removal of the phosphate protecting group was carried out by oxidation of V to the sulfone ester followed by alkaline treatment as described for the phosphate protected mononucleotide. The dinucleotide pTpC^{An}OH was isolated in 80% yield and was homogenous as judged by tlc and paper chromatography.

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Preparation, Properties, and Structure of a Diamagnetic Dimeric Diiron Compound with Three Bridge Hydrogen Bonds

Sir:

It has been reported[1,2] that the tripod-like triphosphine $MeC(CH_2PPh_2)_3$ (P_3) reacts with cobalt(II) and nickel(II) halides either alone or in the presence of sodium borohydride to give tetrahedral complexes $M(P_3)X$ in which the oxidation state of the metal is +1.

Iron(II) halides react with the triphosphine under

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