species of significance here are $SCN^-$ and $H(SCN)_2^-$ ions. Under these mild conditions, no ions originating from the polymeric matrix are observed. Figure 2b is a similar spectrum of ammonium fluoroborate exhibiting only the $BF_4^-$ ion. Ammonium nitrate, shown in Figure 2c, produces only $NO_3^-$ and $HNO_3 \cdot NO_3^-$ ($HN_2O_6^-$) ions. Ammonium persulfate, Figure 2d, shows, interestingly enough, $HS_2O_7^-$ and $HSO_4^-$ in addition to $HS_2O_8^-$ ions rather than the double charged anions.

The formation of uncomplexed or merely protonated anions is not specific to ammonium salts and seems to occur with oxyanions that do not form complexes with metallic cations. Thus, sodium perchlorate, shown in Figure 3a, shows only $ClO_4^-$ ions plus a few $H(ClO_4)_2^-$ ions, similarly to the ammonium salts described above. Under more drastic conditions (130°C, 2.5 kV), sodium sulfate was shown to produce $SO_4^{2-}$ in addition to $HSO_4^-$, as shown in Figure 3b. We could not identify some of the additional negative ions formed under these conditions, probably because of the action of sulfuric acid on the polyalcohol. A rather interesting case is the spectrum of $Na_3FeF_6$ in Figure 3c. Here we were able to identify $FeF_6^{3-}$ in addition to $HFeF_5^{2-}$, $FeF_3^-$, $FeF_4^-$, and $NaHFeF_6^-$. Figure 3d shows the spectrum of uranium tetrafluoride suspended in the PVA matrix. The predominant uranium ion formed under fairly mild conditions (~2 kV) is $UOF_5^-$ and its hydrate $UOF_5H_2O^-$. Moreover, $UF_6 \cdot OH \cdot H_2O^-$ ions in a small yield also seem to appear in the spectrum. The latter two spectra suggest that negative ion desorption may be a highly useful tool in the study of the nature of anionic complex ions.

Although the spectra reported in this communication are only preliminary qualitative results, they demonstrate well the potential of negative ion desorption mass spectrometry for the analytical and inorganic chemist.

### References and Notes

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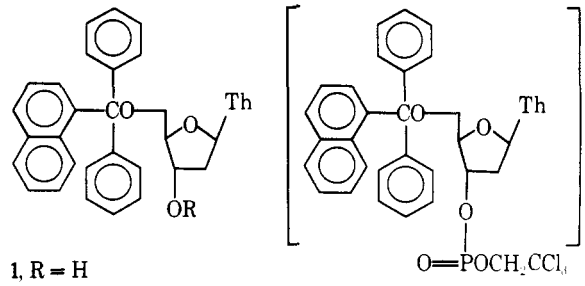
## Selective Deprotection by Reductive Cleavage with Radical Anions[1]

*Sir:*

We describe in this communication the selective removal of α-naphthyldiphenylmethyl, a new protecting group, from 5′-*O*-α-naphthyldiphenylmethyl-3′-*O*-*p*-methoxytritylthymidine (**2**) by reductive cleavage with the anthracene radical anion in tetrahydrofuran (THF). This reaction illustrates a technique for selective deprotection which should be generally useful in synthetic work with polyfunctional compounds.

Selectivity in cleaving members of a family of protecting groups has most often depended on differences in rates of reaction with basic, nucleophilic, or acidic reagents. Examples include the sequential hydrolysis of phenoxyacetic, acetic, and trimethylacetic esters[2] under alkaline conditions and the selective hydrolysis of *p*-dimethoxytrityl[3] ethers in the presence of trityl ethers in acidic media. Recently electrolytic reduction has been exploited to discriminate among haloethoxycarbonyl protecting groups.[4]

The successful utilization of the naphthalene radical anion in cleaving methoxytrityl[5] and trichloroethylphosphoryl[6] derivatives of thymidine without reduction of the base ring pointed up the possibility of developing a technique for controlled stepwise removal of protecting groups based on radical anion chemistry. To test this possibility, thymidine derivatives protected at 5′-O by α-naphthyldiphenylmethyl were prepared (compounds **1**–**3**), with the expectation that the naphthalene ring would serve as a better electron acceptor than phenyl or *p*-anisoyl. Compound **1**[7] was obtained (65%) by reaction of α-naphthyldiphenylmethyl chloride[8] with thymidine in pyridine. It was converted to **2**[7] (92%) by reaction with *p*-methoxytrityl chloride in pyridine and to **3**[7] (97%) by successive treatment with trichloroethylphosphorodichloridite in tetrahydrofuran–lutidine and iodine–water.[6,9]



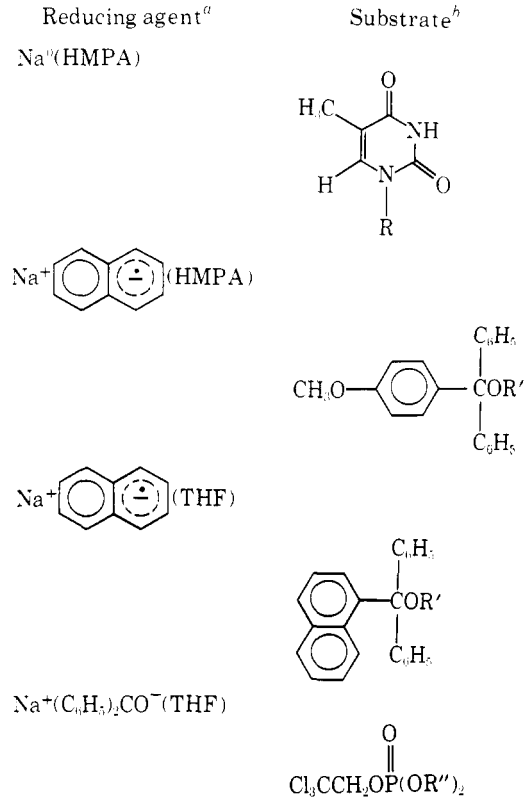

1, R = H
2, R = $CH_3OC_6H_4C(C_6H_5)_2$
3

Solutions differing in reduction potential were prepared by stirring 1.2 mmol of naphthalene, anthracene, or benzophenone with 1 mmol of sodium in 4 ml of tetrahydrofuran (1 hr) or in hexamethyl phosphoric triamide (HMPA) (4 hr)[10] at room temperature. The nucleoside derivative (0.01–0.1 mmol) was added and, after 10 min, the reaction was quenched by addition of water. Following neutralization with acetic acid, the solution was extracted several times with chloroform. Thymidine (aqueous layer) was determined spectrophotometrically. Chloroform-soluble nucleosides and nucleotides were isolated by chromatography on silica plates.

Reaction of the naphthalene radical anion in HMPA afforded, as expected,[5] thymidine from both 5′-*O*-*p*-methoxytritylthymidine (90%) and compound **1** (91%). The yield of thymidine was considerably lower (34–40%) when THF was employed as the solvent. Reduction of the triarylmethyl ethers was complete in THF, as indicated by the absence of products that gave a positive test with perchloric acid; however, additional products resulting from side reactions were observed on the silica plates used for analysis.[11] It was found that the activity of this radical anion in THF could be moderated by adding a small amount of HMPA to the mixture. With a solvent consisting of seven parts THF and one part HMPA (v/v) high conversion to thymidine was realized (92–94% for both **1** and 5′-O-*p*-methoxytritylthymidine).[12]

A solution of the anthracene radical anion in THF proved to be an excellent system for discriminating between the *p*-methoxytrityl and α-naphthyldiphenylmethyl protecting groups. Compound **1** was converted to thymidine in high yield (97%) whereas 5′-*O*-*p*-methoxytritylthymidine was essentially inert under the reaction conditions (2% thymidine). The difference in reactivity of the α-naphthyldiphenylmethyl and the *p*-methoxytrityl protecting groups was confirmed by treating **2** with the anthracene radical anion reagent in THF. 3′-*O*-*p*-Methoxytritylthymidine was isolated from this reaction in 87% yield (cleavage of the α-naphthyldiphenylmethyl group) and the yield of thymidine was only 3% (cleavage of both protecting groups). It may be

Chart I. Order of Reductive Cleavage of Protecting Groups




[a] HMPA, hexamethylphosphoric triamide; THF, tetrahydrofuran. [b] The thymine ring is reduced; in the other cases the indicated protecting groups are removed.

noted that the relative reactivity of these triarylmethyl derivatives toward radical anions is the reverse of that toward acid.[13]

Further differentiation in deprotecting was observed with the benzophenone radical anion in THF. This agent was relatively unreactive toward the *O*-α-napthyldiphenylmethyl group (only 4% of thymidine was obtained from **1**); but it was sufficiently active to remove the β,β,β-trichloroethyl group from trichloroethylphosphotriester derivatives. Thus **3** in tetrahydrofuran was converted to 5′-*O*-α-naphthyldiphenylmethylthymidylyl[3′-3′]-5′-*O*-α-naphthyldiphenylmethylthymidine, which was isolated in 88% yield. Control experiments showed that the anthracene radical ion converted **3** to thymidyly[3′-3′]thymidine and that the benzophenone radical anion failed to react with **2**.

The relative reactivity of the radical anions toward these protected nucleosides is summarized in Chart I. A given reducing agent reacts efficiently with those substrates lying below it in the chart and reacts very little with those lying above it. It is reasonable to expect that the chart can be expanded to include a number of other reducing agents, protecting groups, and classes of polyfunctional compounds.

## References and Notes

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(11) In contrast, sodium naphthalene in THF is reported to cleave the benzyl group from *N*-benzyluridine without complications; K. D. Phillips and J. P. Horwitz, *J. Org. Chem.*, **40**, 1856 (1975).
(12) The concentration of HMPA is approximately 1 *M*. This reaction is therefore more sensitive to added HMPA than the alkylation reaction investigated by E. J. Panek, *J. Am. Chem. Soc.*, **95**, 8460 (1973).
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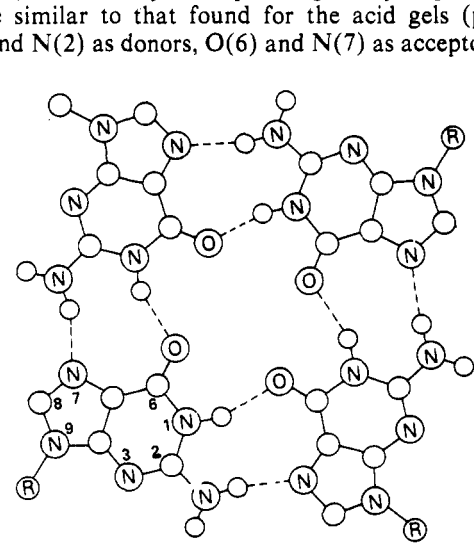
## Self-Assembled 5′-Guanosine Monophosphate. Nuclear Magnetic Resonance Evidence for a Regular, Ordered Structure and Slow Chemical Exchange

*Sir:*

Among all of the nucleic acid components, guanosine monophosphate (GMP) possesses a unique ability to undergo spontaneous formation of a regular, ordered structure in aqueous solution. This property is manifested in part by the formation of anisotropic acid gels[1-6] (pH ~5) in which the bases are hydrogen-bonded to form continuous helixes (5′-isomer)[7] or planar tetramer units which stack in a helical array (3′-isomer).[1] The 5′-isomer also forms an ordered structure in neutral solution (pH 7-8),[8] but it is distinguished from the acid structure by lack of gel formation, different ir properties, a more cooperative melting profile, and a lower transition temperature. It has been proposed on the basis of ir and chemical evidence[8] that the neutral structure consists of helically arranged stacks of planar tetramer units (**1**) formed by incorporating a hydrogen-bonding scheme similar to that found for the acid gels (positions N(1) and N(2) as donors, O(6) and N(7) as acceptors).



We now wish to report NMR evidence for a regular, ordered structure and slow chemical exchange for self-assem-