

with methanol was repeated, and the residue was then suspended in 1 ml. of methanol and 0.05 ml. of triethylamine, which was removed under high vacuum. This residue was dissolved in H₂O and examined by paper chromatography (solvent A), paper electrophoresis, and by the standard hydrolytic derivatization reactions.

Approximately 80% of the starting material reacted to give two products, separated in solvent A (*R_f* 0.10 and 0.45, compared with 0.34 for starting material) in the ratio of about 2:1. On paper electrophoresis all nucleotidic material moved in a long spot slightly slower than the starting material (Table I) which corresponded, nevertheless, to a dianion. Hydrolysis with NH₄OH gave Guo-5'-P and 2'-O-THP-Guo-5'-P, again in about 2:1 ratio; with HOAc yielded unchanged *R_f* 0.10 material as well as N-benzoyl-Guo-5'-P; and with both acid and base gave Guo-5'-P. These results suggested that either the THP group was partially removed during the reaction or work-up or that hydrolysis of this group was very much slower in the *R_f* 0.10 material than in the starting nucleotide. The changes in the *R_f* 0.45 material are consistent with its being the desired N-benzoyl-2'-O-THP-3'-O-acetyl-Guo-5'-P, but this identification can only be considered tentative.

N-Benzoyl-2'-O-tetrahydropyranyl-5'-O-(2''-cyanoethyl)phosphorylguanosine. An aqueous solution containing 36 μmoles of triethylammonium N-benzoyl-2'-O-THP-Guo-5'-P was rendered anhydrous and the dry solid mixed with 14 ml. (208 mmoles) of 3-hydroxypropionitrile giving a clear solution. A mixture of this solution with 72 mg. (350 μmoles) of DCC was agitated for 5 min. to dissolve the reagent and then allowed to stand 96 hr. at room temperature. The reaction was stopped by the addition of 16 ml. of H₂O. Because dicyclohexylurea is appreciably soluble in aqueous 3-hydroxypropionitrile, the reaction mixture was then diluted to about 200 ml. with H₂O, filtered, and the residue thoroughly washed with water. The filtrate and washes were mixed with an aqueous suspension of several grams of DEAE cellulose (HCO₃⁻) (to bind the nucleotides) which was then filtered. The DEAE cellulose was washed with water until the filtrate no longer gave a precipitate when mixed with excess NaOH, indicating the absence of 3-hydroxypropionitrile, and then eluted with 0.1 M triethylammonium bicarbonate until the absorbance at 260 mμ

fell to a low value.²⁰ The buffer was removed in the usual way, and the product was dissolved in H₂O and characterized.

Two spots of N-benzoylguanosine derivatives were observed on paper using solvent A, the major one (80% of total nucleotide present) at *R_f* 0.53 and another at *R_f* 0.79. A small amount of a substance, tentatively identified as 2'-O-THP-5'-O-(2''-cyanoethyl)phosphorylguanosine, was also observed at *R_f* 0.38; this material probably arose by hydrolysis of the benzoyl group during removal of triethylammonium bicarbonate. The principal product resulting from NH₄OH hydrolysis of the aqueous product mixture was 2'-O-THP-Guo-5'-P, though traces of other nucleotides were also observed (also see ref. 13). With acetic acid hydrolysis, the principal product was N-benzoyl-Guo-5'-P; a new substance, in small amounts, tentatively identified as N-benzoyl-5'-O-(2''-cyanoethyl)phosphorylguanosine was also detected. As expected Guo-5'-P was the product of sequential acid and alkaline hydrolyses. Paper electrophoresis at pH 8.5 also showed that all nucleotide material in the product mixture was diesterified. The spectrum of the aqueous product mixture was close to that of the other N-benzoylguanosine derivatives studied, though the *A₂₉₀/A₂₆₀* ratio was reduced slightly indicating about 10% hydrolysis of the N-benzoyl group, in accord with the chromatographic results. The yield of total nucleotide, of which about 80% was the desired compound, based on total phosphorus was 18.9 μmoles (53%).²¹ Since no starting material was detected in these characterizations, all losses must have occurred in purification steps.

Acknowledgments. The author wishes to acknowledge the expert technical assistance of Marianne Byrn and Mrs. Jean Mahoney and express his thanks to Professor Jacques R. Fresco who provided the facilities for the experimental work reported and who gave continued support, encouragement, and pertinent advice throughout the course of this work.

(20) The elution of the nucleotide product in this experiment was inefficient due to the relatively low anion concentration of the eluent, and to the uniform distribution of nucleotide on the exchanger occurring in the batchwise sorption procedure. In later syntheses this step was carried out on columns with resultant increased efficiency and higher recovered yields.

(21) In another synthesis, identical with this one except for column rather than batchwise purification on DEAE cellulose,²⁰ an 80% yield of diesterified nucleotide was recovered.

Communications to the Editor

Fluorenyllithium-Lewis Base Complexes

Sir:

It has been known for some time from anionic polymerization¹⁻⁴ and other studies^{5,6} that organolithium

- (1) A. V. Tobolsky and C. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959).
- (2) R. S. Stearns and L. E. Forman, *ibid.*, **41**, 381 (1959).
- (3) S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962).

compounds complex with Lewis bases and the reactivity of the resulting complexes is significantly different from that of the respective uncomplexed RLi. However, little

(4) D. L. Glusker, R. A. Galluccio, and R. A. Evans, *J. Am. Chem. Soc.*, **86**, 187 (1964).

(5) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963).

(6) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *ibid.*, **84**, 1371 (1962).

Table I. N.m.r. Chemical Shifts of Complexed Fluorenyllithium

RLi	Base	Solvent	Fluorene nucleus ^a				Base ^a		Cation ^b Li ⁷	Ratio, Base/ RLi	
			Singlet 9-proton	Quartet 2,3,6,7	Quartet	Doublet 1,8	Doublet 4,5	α - or CH ₂ protons			β - or CH ₃ protons
...	THF	C ₆ H ₆	3.61	1.51
Fl-THF complex	THF	THF	5.80	6.30	6.72	7.20	7.78
Fl-THF complex	THF	C ₆ D ₆	6.00	6.91	7.25	7.65	8.24	2.81	1.23	-3.0	3:1
...	DME	C ₆ H ₆	3.38	3.18
Fl-DME complex	DME	DME	5.87	6.32	6.72	7.21	7.78
Fl-DME complex	DME	C ₆ D ₆	6.27	7.04	7.36	7.80	8.35	2.16	2.42	...	1.2:1
Fl-Et ₂ O complex	Et ₂ O	Et ₂ O	5.76	6.66	6.98	7.40	7.98	-6.2	...

^a Chemical shifts in p.p.m. downfield from tetramethylsilane. ^b Chemical shifts in p.p.m. upfield from a 20% aqueous solution of lithium chloride.

is known about the structure of such complexes, and there are areas of disagreement.^{5,6} As a portion of an investigation of organolithium-Lewis base complexes we have examined the proton n.m.r. spectra of fluorenyllithium-tetrahydrofuran (Fl-THF), fluorenyllithium-dimethoxyethane (Fl-DME), and fluorenyllithium-diethyl ether (Fl-Et₂O) complexes in the respective ethereal solvent systems, the proton n.m.r. spectra of Fl-THF and Fl-DME complexes in benzene-*d*₆, and the Li⁷ n.m.r. spectra of Fl-THF and Fl-Et₂O.

Fluorenyllithium-THF and -DME complexes were prepared from fluorene and lithium metal in THF or DME, precipitated by addition of heptane, filtered, washed, and dried under vacuum (<1 mm.) for 48 hr. For the preparation of the Fl-Et₂O solution, fluorene and *n*-butyllithium were allowed to react in heptane. The solid fluorenyllithium was filtered, washed with heptane, dried under vacuum, and dissolved in ether. Solutions of the yellow crystalline complexes in benzene, benzene-*d*₆, or the respective base were used for the proton n.m.r. measurements. The chemical shifts are tabulated in Table I. The following observations were made.

(1) THF and DME remain complexed with fluorenyllithium after drying for 48 hr. under vacuum (<1 mm.) at room temperature. Integrations of the spectra indicate a mole ratio of THF to RLi of 3.0-3.2/1.0 and of DME to RLi of 1.2-1.3/1.0.

(2) The resonance due to the 9- or benzylic proton in fluorenyllithium is found approximately 3 p.p.m. downfield from its position in the spectrum of fluorene and the aromatic protons are resolved into two doublets and two quartets, assignable on the basis of splitting and integration to the 1- and 4-protons and the 2- and 3-protons, respectively. These results agree with observations of Schaefer and Schneider⁷ of the n.m.r. spectrum of fluorenylsodium. The chemical shifts of the protons in fluorenyllithium are sensitive to the nature of the complexing Lewis base and to the solvent system.

(3) The α - and β -protons of the complexed THF are shifted appreciably upfield from the uncomplexed base. Similarly, the methyl and methylene protons of the complexed DME also are shifted appreciably upfield and, in addition, their relative positions are reversed.

(7) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

In contrast, Eastham and co-workers⁵ observed a downfield shift of the α -protons of diethyl ether of 0.2 p.p.m. when it was complexed with *n*-butyllithium.

(4) The Li⁷ n.m.r. signals of fluorenyllithium-diethyl ether in ether solvent and of fluorenyllithium-THF in benzene solvent occur at 6.24 and 3 p.p.m., respectively, upfield from a 20% aqueous lithium chloride solution. This is strikingly different from the results obtained with alkyl, aryl, and alkenyl organolithium compounds observed in this and other laboratories,⁸⁻¹⁰ wherein the signals were found between 1.74 p.p.m. downfield (*n*-butyllithium) and 0.41 p.p.m. upfield (allyllithium) from aqueous lithium salt solutions as standards.

It seems reasonable that Lewis acid-base interactions of RLi and an ether might deshield the α -protons of the ether, either by increasing the electronegativity of the oxygen⁵ or by an inductive effect of the electrophilic⁶ organolithium reagent. On the other hand, it is difficult to invoke any resonance or inductive interaction between fluorenyllithium and base that would explain our findings of an upfield shift of the α -protons of THF and DME, the shifting of not only the α - but also the β -protons of THF, the reversing of the relative positions of the methyl and methylene protons of DME, and finally the appearance of the Li⁷ signal strongly upfield from the Li⁷ resonance of lithium aluminum hydride.⁸ We believe, however, that the following postulates explain the n.m.r. proton and lithium cation data and are consistent with all other available data.^{11,12}

The lithium cation is located directly above the plane of the aromatic carbanion, possibly in the π cloud. It is not intimately associated with the 9- or benzylic carbon in (or near) the ring plane and is not located on the periphery of the ring system. In addition the base molecules, which are strongly coordinated with the cation, are also located above the fluorenyl carbanion. As a consequence, both the cation and base are in the magnetic field due to the ring current. This magnetic

(8) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964).

(9) M. A. Weiner and R. West, *ibid.*, **85**, 485 (1963).

(10) D. C. Lini, J. A. Dixon, and R. A. Bernheim, unpublished results.

(11) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

(12) A. Streitwieser, Jr., W. M. Padgett, II, and I. Schwager, *J. Phys. Chem.*, **68**, 2922 (1964).

field opposes the applied magnetic field directly above and below the aromatic ring and thus produces the observed strong shielding effect on the protons of the base and the lithium cation.

Acknowledgment. We gratefully acknowledge the generous support of the American Petroleum Institute and the Socony Mobil Oil Company, a fellowship to one of us (D. L.) from the Shell Oil Company, and a grant from the National Science Foundation for the purchase of the spectrometer. The proton n.m.r. spectra were obtained by Mr. D. O. Lauver. In addition, we wish to thank Drs. R. A. Bernheim and N. A. Matwiyoff for helpful discussions.

Joseph A. Dixon, Paul A. Gwinner, David C. Lini
Whitmore Laboratory, College of Science
The Pennsylvania State University, University Park, Pennsylvania
Received December 23, 1964

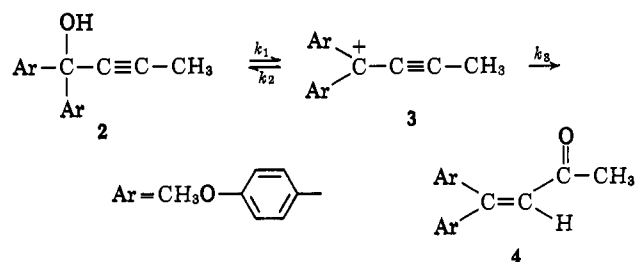
Alkynyl Cations

Sir:

This communication reports the first direct observations of alkynyl cations (**1**). A particularly interesting aspect of these cations is that they can also be regarded as vinyl cations if resonance structure **1b** is important.



Solutions of propynyl-di-*p*-methoxyphenylcarbinol^{1,2} (**2**) in concentrated sulfuric acid exhibited λ_{max} 518 $m\mu$ (ϵ 43,000), indicating that a new absorbing species



had formed. Careful introduction of **2** into concentrated sulfuric acid by extraction from carbon tetrachloride gave solutions that exhibited the simple n.m.r. spectrum³ shown in Figure 1. This spectrum is assumed to be due to carbonium ion **3**; the assignment for each band is indicated in the figure. Structure **3** for the new species in the solutions seems reasonable because of the close correspondence of the positions of the bands due to the *p*-methoxyphenyl group with those of other *p*-methoxyphenyl-substituted carbonium ions.⁵ Strong confirmation of structure **3** was obtained by recovery of the starting alcohol (**2**) on neutrali-

(1) This alcohol was prepared by addition of propynyllithium to di-*p*-methoxyphenyl ketone.

(2) A satisfactory analysis was obtained for this new compound.

(3) Chemical shifts are expressed in p.p.m. relative to tetramethylsilane as 10.00. Tetramethylammonium chloride, used as an internal reference in the sulfuric acid solutions, was assumed to absorb at 6.90 p.p.m.⁴

(4) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

(5) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959); P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); H. G. Richey, Jr., unpublished observations.

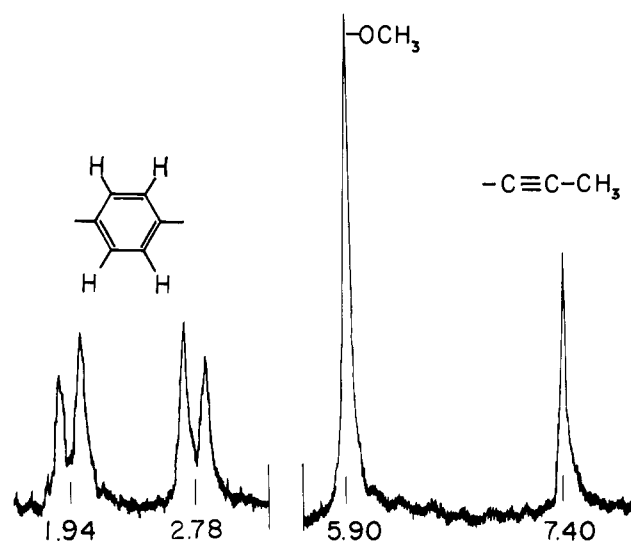


Figure 1. N.m.r. spectrum of a sulfuric acid solution of cation **3**.

zation of the sulfuric acid solutions by their careful addition to aqueous sodium hydroxide using a rapid dispersal technique. The recovered products, obtained in yields of about 90%, consisted principally of alcohol **2**, though an isomer, ketone **4**,^{2,6} always constituted at least 10% of the product. This ketone formed almost quantitatively when dilute perchloric acid was added to an acetone solution of **2**. Under conditions that allow equilibrium to be reached, **4** is the product formed from reaction of water with solutions of the ion; however, irreversible reaction of the ion with water leads principally to **2**, so k_2 must be larger than k_3 .

The n.m.r. absorption of the propynyl methyl group of ion **3** is considerably downfield from the absorption at 8.13 p.p.m. exhibited by this group in a carbon tetrachloride solution of **2**. This is probably a result of significant delocalization of charge into the propynyl group as suggested by resonance structure **1b**. The basicity of **2**, which would indicate the effect of delocalization into the propynyl group on stabilization of cation **3**, could not be measured directly because of the rapid disappearance of the ion in more dilute solutions of sulfuric acid, presumably due to attack by water leading to **4**. In 77% sulfuric acid, the half-time for the disappearance of the 518 $m\mu$ absorption of **3** was 45 min. at $\sim 25^\circ$. The disappearance became very much more rapid as the acidity was lowered; in 20–50% sulfuric acid, the concentration range in which the concentrations of **2** and **3** might be expected to become comparable, the color of the ion could be seen but faded within seconds.

Addition either of **5**⁷ or a mixture⁸ of **7** and **8** to concentrated sulfuric acid led to solutions which exhibited the n.m.r. spectrum shown in Figure 2. This

(6) Ketone **4**, b.p. 180–185° (0.12 mm.), formed a 2,4-dinitrophenylhydrazone derivative,² m.p. 181–182°. The n.m.r. spectrum of a carbon tetrachloride solution of **4** exhibited absorptions at 8.27 (singlet, 3 H) for the C-methyl hydrogens, 6.27 (singlet, 3 H) and 6.23 (singlet, 3 H) for the O-methyl hydrogens, 3.68 (singlet, 1 H) for the vinyl hydrogen, and 2.78–3.36 p.p.m. (2 overlapping quartets, 8 H) for the aryl hydrogens.

(7) Alcohol **5**, b.p. 80–85° (2.2 mm.), was obtained by addition of a propynyl Grignard reagent to isophorone.

(8) A mixture of hydrocarbons, b.p. 55–65° (1.7 mm.), of which **7** and **8** are probably the major components, was also obtained by addition of a propynyl Grignard reagent to isophorone.