teins has been considered also by others.[8–12] Imanishi, *et al.*,[12] concluded that detergents facilitated destruction of the β form and promoted formation of the α-helix in Bence-Jones proteins. According to Troitskii,[5] the negative shift of b_0, *e.g.*, of serum γ-globulin, upon treatment with sodium decyl sulfate, is caused not by the formation of the α-helix but by destruction of the β conformation. This contention led to the experiments described in this communication.

Since the conformation of the nonhelical proteins, such as γ-globulin, is unknown, an example of a completely disordered protein should be found. The calf thymus histone fractions at very low ionic strength were found to behave as fully disordered linear polyelectrolytes. At low concentrations of the histone, its reduced specific viscosity increased exponentially with dilution,[13] and its rotatory dispersion curve in the Cotton effect zone of 190–240 mμ was very similar to the curve of the disordered poly-α-L-glutamate.[14,15] While some histone fractions, *e.g.*, F2b, became partially α-helical on addition of 0.02 to 0.1 M NaCl or other electrolytes, the lysine- and proline-rich histone F1 did not become ordered on such treatment.[14] To test the helix-forming ability of detergents, 0.10–0.32% aqueous solutions of the lysine-rich histone F1 were treated with 0.0012–0.05 M sodium dodecyl or decyl sulfate at 25° for at least 24 hr or at 50° for 2 hr. Small amounts of the aqueous detergent, when added to the histone solution, produced a precipitate (due to electrostatic interaction between the positively charged macromolecules of the histone with the negatively charged micelles of the detergent), but the precipitate dissolved in an excess of detergent. The dodecyl sulfate was more potent in forming a soluble complex than the decyl sulfate. The conformational transitions were determined by measuring the optical rotatory dispersion in the far ultraviolet with the Rudolph Model RSP-3 spectropolarimeter equipped with a double prism monochromator, as described previously.[14–16]

It was found that both decyl and dodecyl sulfates converted the disordered histone F1 partially into the α-helical form. While the pure aqueous histone displayed curves with a deep minimum at 206 and 209 mμ, the detergent-treated histone had curves with a minimum at 230 to 232 mμ and a positive maximum at 197 to 200 mμ as do proteins having a high α-helix content.[16–19] The results are summarized in Table I. An accurate estimation of the α-helix content is impossible, especially from the amplitude of the negative trough, because factors other than the α-helix are involved.[20,21] If the amplitudes of the positive peak are used,[15] the helix content is $[R']_{198}/75{,}000$, *i.e.*, 19,000/75,000 or 25%. Circular dichroism studies have shown that the rotational strength of the 190-mμ transition is about four times greater than that of the 222-mμ transition.[22] This favors the $[R']_{198}$ values for the estimation of the α-helix content. The b_0 values of the detergent-treated histone were between −157 and −190°, as determined from measurements in the 240- to 300-mμ zone using a λ_0 of 216, whereas the b_0 of the aqueous F1 was near zero. The other lysine-rich histone fraction F2b, which could be made 20% helical by NaCl and other simple electrolytes,[14] was converted to 36% α-helical form by a similar treatment with dodecyl sulfate. This higher efficiency of the detergent can be explained by the lesser content of proline in F2b (3.4%) in comparison to the 9.4% in F1. Complete amino analyses of the histones used have been reported.[14]

Table I. Cotton Effect Amplitudes of Histone F1 Treated with Decyl or Dodecyl Sulfates[a]

Mole ratio, F1 : detergent	Time, hr, and temp, °C, of treatment	$[R']^{25}_{231}$, deg	$[R']^{25}_{198}$, deg
1:5000 C_{10}	24, 25	−4500 (±500)	+17,800 (±1500)
1:5000 C_{10}	2, 50	−4900	+18,500
1:5000 C_{12}	2, 50	−6500	+18,000
1:1250 C_{12}	2, 50	−6500	+19,200
1:250 C_{12}	2, 50	−5300	+18,600
1:125 C_{12}	2, 50	−5700	+16,300

[a] The molecular weight of F1 was approximately 20,000. The $[R']$ values were computed from $[R'] = [\alpha]3M/100(n^2 + 2)$, where $[\alpha]$ is the specific rotation, M the mean residual molecular weight of the amino acids, and n the refractive index of the solvent. An approximation of $[R'] = 0.9[\alpha]_{231}$ and $[R'] = 0.85[\alpha]_{198}$ was used.

The observations prove that decyl and dodecyl sulfates do indeed facilitate the α-helix formation. The mechanism of this interaction is unknown, but it is likely that the bound detergent provides a hydrophobic environment around the peptide bonds, thus protecting them from hydrogen bonding with water.[23] These observations do not disprove the claim of other investigators[5,11] that detergents destroy the β structure. However, it seems that this is not the only transition the detergents are able to incite. Since the disordered histones are converted in part into the α-helical form, it is possible that the same may happen in some other proteins.

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A Novel Method for the Formation of the Tetraphenylbismuthonium Cation

Sir:

The metathetical reaction between silver salts and organometallic chlorides, bromides, or iodides to form a variety of organometallic compounds has been widely used for preparative purposes. In earlier work[1,2] we employed this reaction to synthesize a number of compounds of types R_3SbY_2 and $(R_3SbY)_2O$. Thus triphenylantimony difluoride was formed when triphenylantimony dichloride was treated with 2 equiv of silver fluoride. However, when 2 equiv of silver perchlorate were used in place of the fluoride, the resulting product was oxybis(triphenylantimony) diperchlorate. We therefore anticipated that reaction between triphenylbismuth dichloride and 2 equiv of silver perchlorate would yield oxybis(triphenylbismuth) diperchlorate or possibly triphenylbismuth diperchlorate. When the filtrate from the mixture was concentrated, however, the product which crystallized proved to be *tetraphenylbismuthonium perchlorate*. That this was indeed the product was shown by: (a) elementary analysis, (b) comparison of the product with a sample of tetraphenylbismuthonium perchlorate prepared by a known method,[3] and (c) conversion of the product to the tetraphenylborate derivative and comparison of this derivative with tetraphenylbismuthonium tetraphenylborate prepared by a known method.[3] The formation of a tetraphenylbismuthonium compound from triphenylbismuth dihalide is remarkable since metathesis between triarylbismuth dihalides and silver salts has been used many times previously without this unusual structural change being observed.[4,5]

It is not easy to write, *a priori*, a mechanism for this reaction in which a phenyl–bismuth bond is broken and another phenyl–bismuth bond is formed at room temperature. The synthesis has been repeated a number of times, and a yield in the neighborhood of 65% (based on phenyl groups) was consistently obtained. This relatively large yield indicates that the tetraphenylbismuthonium perchlorate is not just a by-product of a radical-type reaction.

This reaction is of considerable interest since it represents a comparatively simple route to the preparation of the tetraphenylbismuthonium group. By analogy with the arsonium and stibonium compounds, the tetraphenylbismuthonium cation may prove to be valuable as a precipitant in analytical chemistry. Only a few bismuthonium compounds are known. It was long believed that such compounds were incapable of existence and they have been described only once previously,[3] a preparation which involved a long and difficult pathway through pentaphenylbismuth.

In a typical experiment a solution of 3.250 g (0.0156 mole) of silver perchlorate in 10 ml of absolute alcohol was added to a solution of 4.000 g (0.00782 mole) of triphenylbismuth dichloride in 50 ml of acetone. All of the chloride immediately precipitated as silver chloride. The filtrate was concentrated to 20 ml *in vacuo* at room temperature and was then allowed to stand overnight. The next morning a crystalline product had formed which was removed by filtration and washed with cold absolute alcohol. The yield of crystalline product was 1.504 g. Addition of 100 ml of water to the filtrate resulted in the precipitation of a further 0.874 g of product which had an infrared spectrum very similar to that of the first crop of crystals. The two precipitates were combined (2.378 g, 65.7% yield based on phenyl groups) and recrystallized twice from absolute ethanol.

Anal. Calcd for $C_{24}H_{20}BiClO_4$: C, 46.73; H, 3.27; Cl, 5.75. Found: C, 46.31; H, 3.35; Cl, 5.95.

The infrared spectrum of the above compound was determined in the region between 4000 and 250 cm^{-1} and found to be identical with the spectrum of tetraphenylbismuthonium perchlorate prepared by Wittig's method.[3] Infrared spectra were determined for Nujol mulls between CsBr plates with a N_2-purged Perkin-Elmer Model 521 infrared spectrophotometer. The observed bands may be divided into three groups of frequencies: (a) assigned to the phenyl: 1564 (m), 1471 (s), 1436 (s), 1328 (m), 1307 (vw), 1190 (m), 1062 (m), 1052 (m), 1012 (w), 992 (s), 734 (s), 686 (m), 609 (w), 442 (m), and 432 (m); (b) assigned to the perchlorate ion: 1090 (s) (broad), 916 (w), 624 (m), and 456 (vw); and (c) unidentified: 996 (m), 846 (vw), and 652 (w).

When a sample of the product was dissolved in absolute alcohol and warmed with an equimolar portion of sodium tetraphenylborate, a voluminous white precipitate was obtained. Recrystallization from nitromethane resulted in a material melting at 215°, which is 10° lower than the tetraphenylbismuthonium tetraphenylborate reported by Wittig.[3] However, by Wittig's method we were unable to prepare tetraphenylbismuthonium tetraphenylborate which had a melting point higher than 217°. Furthermore, the melting point of the compound prepared from our sample of tetraphenylbismuthonium perchlorate was not depressed when admixed with the material obtained by Wittig's procedure. The melting points were determined on a Fisher–Johns melting point apparatus calibrated against U.S.P. melting point standards.

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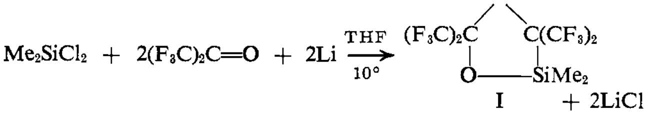
Alkoxysilanes Derived from Hexafluoroacetone. The Purported Intermediacy of Dimethylsilene

Sir:

The following reaction involving the intermediacy of dimethylsilene ($Me_2Si:$) was recently reported.[1]



$$Me_2SiCl_2 + 2(F_3C)_2C{=}O + 2Li \xrightarrow[10°]{THF} \text{I} + 2LiCl$$

The possibility of an alternative structure *via* the relatively conventional bimolecular reduction[2] of the ketone

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