N-Phosphoranylidene Sulfone Iminium Salts

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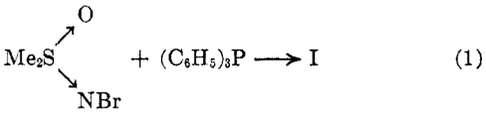
Prompted by Appel's recent report[1] on the preparation of $[(C_6H_5)_3P{=}N{=}S(O)Me_2]^+Br^-$ (I), we wish to describe our closely related but independent work on the synthesis and characterization of two totally aliphatic derivatives by a different synthetic approach.

Appel obtained I by the routes shown in eq 1 and 2.



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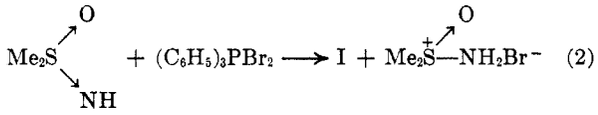
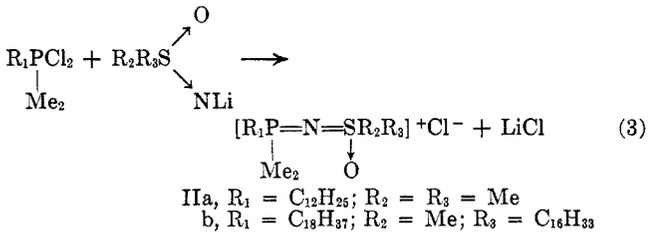


(2)

He has also prepared[2] the related compounds of general structure $[R_3P{=}N{=}SR'_2]^+Cl^-$.

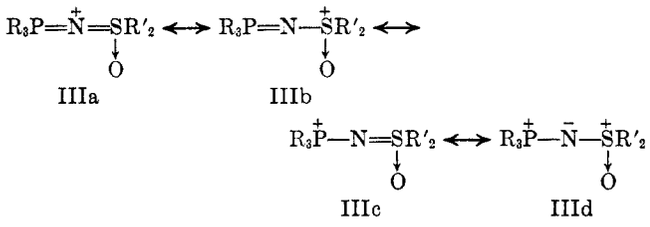
In the present work, the aliphatic N-phosphoranylidene sulfone iminium salts[3] (II) were prepared as shown in eq 3. The functional centers of the salts IIa and IIb



(3)

IIa, $R_1 = C_{12}H_{25}$; $R_2 = R_3 = Me$
b, $R_1 = C_{18}H_{37}$; $R_2 = Me$; $R_3 = C_{16}H_{33}$

can be represented by the resonance forms below. Un-



IIIa IIIb IIIc IIId

fortunately, it is impossible to assess the relative importance of any of these representations on the basis of the information currently in hand.

The N-lithiosulfone imines[5] used in these syntheses were prepared by treating a benzene solution of the appropriate sulfone imine with 1 equiv of *n*-butyllithium. Evaporation of the solvent yielded in each case a solid which lacked the infrared NH absorption of the sulfone imine, and addition of water to the solid followed by adjustment of the solution pH to 7 regenerated the respective sulfone imine (see the Experimental Section). The chemical shift of the methyl protons in the nmr spectrum of $Me_2S(O)(NLi)$ was shown to be the same (τ 7.8) as that of $Me_2S(O)(NH)$.[6] Importantly, no resonances attributable to the protons of *n*-butyllithium could be detected, thus showing that this reagent had been completely consumed.

The salts IIa and IIb were prepared by adding a benzene solution of the N-lithiosulfone imine to the desired tertiary phosphine dichloride[7] dispersed in benzene under argon at room temperature. Structural assignments were based on spectral and microanalytical data coupled with the identification of hydrolysis products (see below). The nmr spectrum of IIa showed a sharp singlet at τ 6.57 and a doublet (J_{PCH} = 12 cps) of equal area centered at 8.07 attributable to the protons of the two methyl groups on sulfur and the two methyl groups on phosphorus, respectively. Partially superimposed on the doublet was a poorly resolved multiplet arising from the methylene protons adjacent to phosphorus. The remainder of the spectrum consisted of a sharp signal (20 protons) at τ 8.75 and a triplet (three protons) centered at 9.13. These were assigned to the remaining methylene protons and the methyl protons, respectively, of the dodecyl group. The spectrum of IIb exhibited, in addition to the proton resonances of the two long-chain groups, the PMe_2 doublet (J_{PCH} = 12 cps) centered at τ 8.05 and the SMe singlet at 6.32 in the relative ratio of 2:1. The P^{31} nmr spectrum of each salt showed only a single, broad absorption centered at −46 ppm relative to 85% H_3PO_4.

Both IIa and IIb were quite resistant to hydrolysis in neutral hydroxylic media.[8] For example, IIa was recovered unchanged after being either stirred in water for 12 days at 25° or heated in water on a steam bath for 16 hr. However, when hydrolysis was attempted in either acidic (1% HCl in the experiments run) or basic (pH 9 or higher) media, destruction occurred within 16 hr at room temperature. Dimethyldodecylphosphine oxide and $Me_2S(O)(NH)$ (or its HCl salt) were isolated and identified from hydrolysis of IIa; dimethyloctadecylphosphine oxide and $C_{16}H_{33}(Me)S(O)(NH)$ arose from basic hydrolysis of IIb. In no case was a sulfone detected (using gc analysis), thus showing that hydrolytic attack occurred on phosphorus rather than on sulfur.

An attempt was also made to prepare IIa by heating $Me_2S(O)(NH)$ with aminodimethyldodecylphosphonium chloride. However, no reaction occurred between

(1) R. Appel, H. Fehlhaber, D. Hänssgen, and R. Schöllhorn, *Chem. Ber.*, **99**, 3108 (1966).

(2) R. Appel and A. Hauss, *Z. Anorg. Allgem. Chem.*, **311**, 290 (1961).

(3) The name "N-phosphoranylidene sulfone iminium" salt is based on the following considerations. Compounds of the type $R_2S(O)(NH)$ have recently and more acceptably been termed "sulfone imines" [4] in preference to the older name, "sulfoximines," and, therefore, salts of these materials should be called "sulfone iminium" salts. Inspection of the formulas of IIa and IIb shows that they can be looked upon as derivatives of sulfone iminium salts wherein both of the valences emanating from nitrogen are bonded to the phosphorus atom. Since the $R_3P{=}$ moiety is commonly termed a "phosphoranylidene" grouping, the proposed name follows directly. Alternative names, such as "phosphiniminooxosulfonium" salt, which is based solely on the resonance structure IIIb, are, of course, possible.

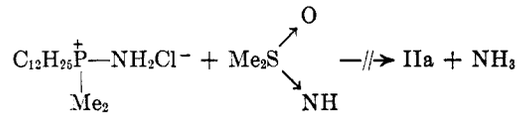
(4) R. G. Laughlin and W. Yellin, *J. Am. Chem. Soc.*, in press.

(5) The preparation of an N-metallosulfone imine, namely $Me_2S(O)(NNa)$, has already been described; see J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952).

(6) Both of these spectra were measured in benzene using TMS as an internal standard so that they could be compared directly while avoiding reaction of $Me_2S(O)(NLi)$ with the more common nuclear magnetic resonance solvents.

(7) The phosphine dichlorides were obtained by adding 1 equiv of gaseous chlorine to the tertiary phosphine; see G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 58.

(8) The hydrolysis experiments were carried out in water for IIa and in aqueous methanol for IIb because of the insolubility of the latter salt in water alone.



the two reagents even when they were heated without a solvent for 17 hr at 125°.

Experimental Section[9]

N-Lithiodimethyl Sulfone Imine.—Dimethyl sulfone imine (mp 56–58°) was prepared as described by Bentley, McDermott, and Whitehead.[10] To a solution of 514 mg (5.52 mmoles) of the sulfone imine in 5 ml of benzene under argon at room temperature was added 4.08 ml (5.52 mmoles) of 1.35 *N* *n*-BuLi. The resulting, milky white liquid was then stirred for 2 hr and evaporated to dryness *in vacuo* (0.5 mm). The infrared spectrum of the resulting, white solid was similar to that of the free sulfone imine except that it lacked the NH absorption and the strong band at 8.3 μ in the spectrum of the latter substance. The solid completely dissolved in 10 ml of water to give a very basic solution. Upon adjusting the solution pH to 7 and evaporating the water, a solid was obtained which was sublimed at 60° (0.1 mm) to give 323 mg (63%) of a light yellow solid. Resublimation yielded white crystals identified as $Me_2S(O)(NH)$ by the identity of its infrared spectrum to that of an authentic sample, and by its melting point and mixture melting point.

N-Lithiohexadecylmethyl Sulfone Imine.—Hexadecylmethyl sulfone imine (mp 70–72°) was prepared using a procedure analogous to that described for its dimethyl analog.[10] Its infrared and nmr spectra were completely consistent with the structure and were essentially identical with those of an authentic sample of dodecylmethyl sulfone imine.[11] A solution of 152 mg (0.5 mmole) of the sulfone imine in 10 ml of benzene under argon at room temperature was treated with 1 equiv of *n*-BuLi, and the resulting, clear solution was stirred for 2 hr. Evaporation of the solvent at 0.5 mm gave a white solid which, as was the case for the dimethyl analog, lacked the NH absorption and the band at *ca.* 8.3 μ in the infrared spectrum of the free sulfone imine. Addition of water gave a basic solution which was adjusted to pH 7 and evaporated to dryness. The resulting solid was extracted twice with chloroform, and the extracts were combined, dried ($MgSO_4$), and evaporated to yield 48 mg (32%) of a solid which, after it was sublimed, was identified as the starting sulfone imine by infrared analysis, melting point, and mixture melting point.

N-(Dimethyldodecylphosphoranylidene) Dimethyl Sulfone Iminium Chloride (IIa).—A solution of 17.8 mmoles of N-lithiodimethyl sulfone imine in 50 ml of benzene was prepared as described above. This was added *via* a syringe to a stirred dispersion of 17.8 mmoles of dimethyldodecylphosphine dichloride[7] in 400 ml of benzene under argon, and the resulting mixture was stirred over night at room temperature. Evaporation of the solvent *in vacuo* gave an oily solid which was partially dissolved by 100 ml of dichloromethane. Centrifugation caused the insoluble lithium chloride by-product to separate, and the remaining, clear, yellow liquid was again evaporated to dryness to yield a gum which slowly crystallized. One recrystallization from 1:1 benzene–hexane gave 4.02 g (63%) of a white solid identified as IIa. (Infrared analysis of the mother liquor clearly showed it to contain more of the same solid.) Several more recrystallizations gave the analytical sample, mp 120–122°. *Anal.* Calcd for $C_{16}H_{37}ClNOPS$: C, 53.68; H, 10.42; Cl, 9.91; N, 3.91; S, 8.96. Found: C, 53.64; H, 10.40; Cl, 9.78; N, 3.63; S, 9.05. The infrared spectrum showed bands at 8.08, 8.54, 9.28, 9.59, 10.27, 10.60, 10.82, and 11.44 μ.

A 307-mg portion of IIa was dissolved and stirred for 5 hr at room temperature in 10 ml of 0.6 *N* NaOH. Evaporation of the solvent *in vacuo* followed by sublimation of the resulting solid gave 163 mg (77%) of white crystals identified as dimethyldodecylphosphine oxide by infrared analysis, melting point, and mixture melting point (undepressed). The residue in the bottom of the sublimer was dissolved in water, and after the solution pH was adjusted to 2 with HCl, the solvent was again evaporated, and the residue was sublimed. A white solid (64 mg, 58%) collected which was identified as $Me_2S^+(O)(NH_2)Cl^-$ by infrared and melting point comparisons to the compound formed by treating $Me_2S(O)(NH)$ with 1 equiv of HCl gas in benzene. Also, a mixture melting point of the two materials was undepressed.

N-(Dimethyloctadecylphosphoranylidene) Dimethyl Sulfone Iminium Chloride (IIb).—To a stirred suspension of 2.53 mmoles of dimethyloctadecylphosphine dichloride[7] in 150 ml of benzene under argon was added 2.53 mmoles of N-lithiohexadecylmethyl sulfone imine in 100 ml of benzene. (The latter solution was prepared as described above.) After the mixture had been stirred for 40 hr at room temperature, the solvent was removed *in vacuo* and 40 ml of dichloromethane was added to the resulting residue. A white solid (IIb) separated which weighed 490 mg (30%) after washing with acetone to remove the LiCl by-product, followed by drying. Several recrystallizations from methanol–acetonitrile gave the analytical sample, mp 143–145°. *Anal.* Calcd for $C_{37}H_{79}ClNOPS$: C, 68.10; H, 12.21; Cl, 5.43; N, 2.15; S, 4.92. Found: C, 67.80; H, 12.26; Cl, 5.22; N, 2.19; S, 4.98. The infrared spectrum was fairly similar to that of IIa and showed absorptions at 8.08, 8.52, 10.31, 10.67, 11.38, 12.50, and 13.93 μ.

A 146-mg (0.22 mmole) portion of IIb was stirred overnight with 0.6 *N* NaOH in 90% aqueous methanol. Evaporation of the solvent *in vacuo* yielded a solid which was sublimed to give 37 mg (54%) of a white solid. This was shown to be $C_{18}H_{37}P(Me_2)(=O)$ by the identity of its infrared spectrum to that of an authentic sample, and by its melting point, and mixture melting point. The residue in the sublimer bottom was dissolved in water, the solution pH was adjusted to 7, and the solvent was evaporated. Sublimation of the residue gave 25 mg (37%) of $C_{16}H_{33}S(Me)(O)(NH)$, as shown by infrared analysis and melting point.

(9) Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 137 Infracord. The proton nmr spectra were obtained using a Varian spectrometer Model HA-100; the spectrum of IIa was measured in deuteriochloroform while that of IIb was measured in CD_3OD–$CDCl_3$. In all cases, TMS was used as an internal standard. Phosphous nmr spectra were recorded on a Varian HR-60 spectromer using benzene (IIa) or methanol (IIb) as solvents. Microanalyses were carried out by Spang Microanalytical Laboratories. *n*-Butyllithium was purchased from Foote Mineral Co. and was titrated immediately before use. All solvents were distilled and dried over molecular sieves. Solids were handled under argon in glove bags purchased from Instruments for Industry and Research, Cheltenham, Pa. Melting points are uncorrected.

(10) H. R. Bentley, E. E. McDermott, and J. K. Whitehead, *Proc. Roy. Soc.* (London), **B138**, 265 (1951).

(11) J. S. Berry, U. S. Patent 3,255,116 (1966); *Chem. Abstr.*, **65**, 5684 (1966).

Registry No.—IIa, 7781-72-8; IIb, 7781-73-9.

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The Reduction of Thiol Esters by Lithium Aluminum Hydride–Aluminum Chloride

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Reductions of thiol esters to sulfides by means of modified lithium aluminum hydride (either by boron trifluoride etherate or aluminum chloride) have recently been reported.[1,2] This report describes the effect of various metal halides as modifiers, and the influence of their molar ratios upon this reaction.

The yields of sulfides are presented in Table I. The data, which reveal that increasing the steric bulk surrounding the thiol ester grouping results in decreased

(1) E. L. Eliel and R. A. Daignault, *J. Org. Chem.*, **29**, 1630 (1964).

(2) D. E. Bublitz, *J. Organometal. Chem.*, **6**, 436 (1966).