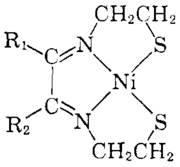
complexes involving the β-mercaptoethylamine grouping.[3] On this basis it is reasonably suggested that the metal ion may bring together the diketone and two moles of mercaptoethylamine in a manner such that the reaction product achieves the predicted form.

When the reactions are carried out in the presence of nickel(II) ion, yields of greater than 70% of the easily purified Schiff base complexes (structure I) are obtained.



I

The complexes which have been prepared are biacetyl-bis-(mercaptoethylimine)-nickel(II), 2,3-pentanedione - bis - (mercaptoethylimine) - nickel-(II), 2,3-octanedione-bis-(mercaptoethylimine)-nickel(II), and 1-phenyl-1,2-propanedione-bis-(mercaptoethylimine)-nickel(II). These compounds shall be abbreviated as Ni(BE), Ni(PE), Ni(OE), and Ni(PPE), respectively.[4]

*Anal.* Calcd. for Ni(BE): C, 36.81; H, 5.41; N, 10.73; S, 24.57. Found: C, 36.74; H, 5.53; N, 10.72; S, 24.37. Calcd. for Ni(PE): C, 39.30; H, 5.86; N, 10.19; S, 23.31. Found: C, 39.34; H, 5.84; N, 10.18; S, 23.19. Calcd. for Ni(OE): C, 45.44; H, 6.99; N, 8.84; S, 20.22. Found: C, 45.31; H, 6.92; N, 8.68; S, 20.02.

The infrared spectra of these complexes show the absence of the strong N–H and carbonyl absorptions, and the presence of a weak absorption corresponding to the stretching vibration of the carbon–nitrogen double bond. This is consistent with the proposed structure. Ni(BE), Ni(PE) and Ni(OE) are diamagnetic, and may therefore be assumed to exist in the expected planar form.

These substances are slightly soluble in a variety of solvents, including benzene, substituted benzenes, halocarbons, alcohols, and water. Molecular weight determinations are hampered by the limited solubilities; however, the measured values agree, within the experimental uncertainties, with the monomer values. *Mol. wt.* Calcd. for Ni(BE), 261; found, 290. Calcd. for Ni(OE), 317; found, 318.

The visible spectra exhibit the usual ligand field transition predicted for *cis*-planar nickel(II).[5] The band occurs at about 430 mμ, in all cases, supporting the expectation that these ligands should exhibit greater ligand field strengths than those associated with nitrogen and oxygen donors. In addition to the ligand field transition, the visible spectra reveal a much more intense absorption maximum which shifts with change of solvent. In the case of Ni(BE) the band maximum ranges from 486 mμ ($H_2O$) to 580 mμ ($CS_2$). The extinction coefficients vary from $1.5 \times 10^3$ to $10^4$. It is apparent that the shift of the band does not correlate with the coördinating ability of the solvent, since, for example, pyridine, a solvent of strong coördinating tendency, produces a shift comparable to that due to the halocarbons, which are very poor coördinating agents. A more successful correlation has been obtained through the use of Kosower's[6] solvent polarity parameter, *Z*. The complete results of these continuing investigations will be published in greater detail elsewhere. The template hypothesis is presently being tested by application to other reactions.

**Acknowledgment.**—The financial support of the National Institutes of Health is gratefully acknowledged.

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[3] D. C. Jicha and D. H. Busch, 135th Meeting of the American Chemical Society, Atlantic City, 1959.

[4] The International Union names for these compounds are, respectively, 2,2'-dimethyl(ethanediylidenedinitrilo)diethanethiolonickel(II); 2 - methyl - 2' - ethyl(ethanediylidenedinitrilo)diethanethiolonickel(II); 2 - methyl - 2' - pentyl(ethanediylidenedinitrilo)diethanethiolonickel (II); and 2-methyl-2'-phenyl(ethanediylidenedinitrilo)diethanethiolo-nickel(II).

[5] G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

[6] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

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## ORGANOSILYL AZIDES

*Sir:*

We wish to report the synthesis of the first organosilicon azides. In common with many other azides,[2-4] these substances were expected to have low thermal stability. Surprisingly, one of these compounds, azidotriphenylsilane (I), is remarkably resistant to heat, being only 50% destroyed after ten hours at 220° in *n*-hexadecane solution. It appears to be more stable to heat than any previously known covalent azide.

The organosilyl azides were prepared from the corresponding chlorosilanes and a sodium azide–aluminum chloride mixture in refluxing tetrahydrofuran. Recrystallization from *n*-hexane gave colorless crystals of I (m.p. 81°) in 90% yield. I is insoluble in water but readily soluble in most organic solvents. *Anal.* Calcd. for $C_{18}H_{15}N_3Si$: C, 71.72; N, 13.94; H, 5.02; mol. wt., 301. Found: C, 71.50; N, 13.89; H, 5.16; mol. wt., 286. Azidophenyldimethylsilane was isolated as a colorless liquid, b.p. 70° (0.15 mm.). It was analyzed by hydrolysis and titration of the liberated hydrazoic acid. *Anal.* Calcd. for $C_8H_{11}N_3Si$: eq. wt., 177.2; found: eq. wt., 176. Azidotrimethylsilane was obtained by a similar reaction using bis-(2-methoxyethyl) ether as solvent. It is a volatile liquid that has to date been isolated only in 90% purity.

Qualitative estimates of hydrolysis rates of the silyl azides in aqueous acetone were made by observing the development of the deep red color of the $Fe^{+3}$-azide complex. All three azides

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285 and grant No. AF-AFOSR-62-244. Reproduction in whole or part is permitted for any purpose of the United States Government.

[2] A. Bertho, *Ber.*, **57**, 1138 (1924).

[3] W. H. Saunders and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

[4] G. Smolinsky, *ibid.*, **82**, 4717 (1960); **83**, 2489 (1961).

hydrolyze more slowly than the corresponding chlorides, their hydrolysis being catalyzed by both acid and base. I hydrolyses very slowly in neutral or basic media, but much more rapidly in acid. Susceptibility to neutral or basic hydrolysis, and also sensitivity to heat, increases with replacement of the phenyl groups of I with methyl groups.

These azides also undergo ready photolysis. I is completely decomposed by prolonged ultraviolet irradiation at 30°. Photolysis and thermal decomposition are believed to occur by the same mechanism as for organic azides,[4,5] namely, through the formation of azene intermediates. The photolytic and thermal decomposition products of I are now under study.

I resembles triphenylmethyl azide in forming an isolable complex with triphenylphosphine.[6] This complex is a high-melting solid. Azidotrimethylsilane also forms a solid with triphenylphosphine.

It seems probable that the unexpected thermal stability of I is due to strong dative pi-bonding from the azide group to silicon. Pi-bonding from the degenerate p orbitals of the alpha nitrogen into the de orbitals of silicon may possibly stabilize a linear Si–N–N–N arrangement, in contrast to the bent structure of organic azides. Similar linear configurations have been reported for the Si–N–C–O system in $Si(NCO)_4$,[7] and the Si–N–C–S system in $H_3SiNCS$.[8] Structural studies of silyl azides are in progress.

(5) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961); R. Huisgen, *Ber.*, **91**, 1, 12 (1958); P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2435 (1951).

(6) J. E. Leffler, U. Honsberg, Y. Tsuno and I. Forsblad, *J. Org. Chem.*, **26**, 4810 (1961).

(7) F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17**, 977 (1961).

(8) D. R. Jenkins, R. Kewley, and T. M. Sugden, *Proc. Chem. Soc.*, 220 (960).

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## CONCERNING THE MECHANISM OF FORMATION OF TRIPHENYLPHOSPHINEALKYLIDENES[1]

*Sir:*

Triphenylphosphinealkylidenes have found widespread application in organic synthesis since the report[2] of their utility in olefin syntheses. The formation of these reagents by the action of bases on triphenylphosphonium salts of type $[(C_6H_5)_3P-\underset{|}{\overset{|}{C}}-H]X$ appears generally believed to involve abstraction of the acidic hydrogen atom $\alpha$ to the phosphonium function by the base.[3]

$$[(C_6H_5)_3PCH_2R]Br + R'Li \longrightarrow (C_6H_5)_3P{=}CHR + R'H + LiBr$$

We have investigated the mechanism of triphenylphosphinemethylene formation and have found that two competing reactions can contribute to the generation of this reagent by the organolithium route. Treatment of 11.2 mmoles of methyltriphenylphosphonium bromide with 10 mmoles of methyllithium in ether gave the usual yellow phosphinemethylene solution. The latter was quenched with 48% aqueous hydrobromic acid, and the organic layer was subjected to gas chromatographic analysis. It was found that benzene had been formed in 26% yield, based on the organolithium reagent. In another experiment the phosphinemethylene reagent formed in this manner was treated with an excess of cyclohexanone, and the volatiles from the reaction were analyzed by gas chromatography. The formation of benzene in 21% yield and methylenecyclohexane in 80% yield was demonstrated. Methyltriphenylphosphonium bromide was treated with ethereal *p*-deuteriophenyllithium in another series of experiments. The resulting solutions (Gilman Color Test I negative) were quenched with 48% hydrobromic acid and with cyclohexanone, respectively. In each case the benzene formed was isolated by gas chromatography. Analysis of the latter (mass spectrometry and falling drop method) showed that in the HBr reaction the benzene was composed of 31% $C_6H_6$ and 69% $C_6H_5D$, in the cyclohexanone reaction, of 28% $C_6H_6$ and 72% $C_6H_5D$. These results indicate that in addition to attack by the lithium reagent on the methyl hydrogens, there occurs to a lesser extent attack at the phosphorus atom of the phosphonium salt. If only attack at the hydrogen atoms were to occur, no benzene would be expected in any of these experiments. If, on the other hand, only attack at phosphorus were to occur, the isolated benzene in the second series of experiments would be expected to be a *ca.* 3:1 mixture of $C_6H_6$ and $C_6H_5D$.

The demonstration that in these reactions attack on phosphorus can occur suggested that it should be possible to generate triphenylphosphinemethylene by the reaction

$$[(C_6H_5)_4P]Br + CH_3Li \longrightarrow (C_6H_5)_3P{=}CH_2 + C_6H_6 + LiBr$$

This was found to be the case. When a suspension of 10 mmoles of tetraphenylphosphonium bromide in a 1:5 diethyl ether–tetrahydrofuran solution of methyllithium (10 mmoles) was heated at reflux, the phosphonium salt dissolved completely, and a reddish-brown solution was formed. Cyclohexanone was added, and the resulting solution was refluxed for 18 hr. Distillation and gas chromatographic analysis of the distillate showed that methylenecyclohexane (identified by its infrared spectrum and refractive index) had been produced in 58% yield, and that benzene had been formed quantitatively in the initial reaction.[4]

Two possible mechanisms may be envisioned for phosphinemethylene formation involving attack on phosphorus: (1) formation of a pentacovalent phosphorus intermediate, followed by its decomposition to the observed products

(1) Studies in Phosphinemethylene Chemistry, Part VI. For Part V see D. Seyferth, J. K. Heeren and S. O. Grim, *J. Org. Chem.*, **26**, 4783 (1961).

(2) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

(3) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(4) It has been reported[2] that this reaction did not occur when these reactants were shaken at room temperature in diethyl ether alone during 4 months. Our conditions (maintaining the 5:1 tetrahydrofuran–diethyl ether solvent system at reflux and high speed stirring) apparently were sufficiently different to allow this reaction to proceed.