these compounds. The increase in the s character of the Si–N σ bonds on partial rehybridization of the nitrogen atom from sp^3 to sp^2 may also contribute to the hypsochromic shift by increasing the energy of the excited state.[12] Alternatively, the absorption can be attributed to the $\pi \rightarrow \pi^*$ transition of the $(p \rightarrow d)\pi$ Si–N bond, where the ground and excited states are largely n and 3d(Si) in character, respectively. For this situation, the excited state is slightly stabilized (because of an averaging of the perturbation) while the ground state becomes substantially stabilized by the progressive introduction of silicon atoms.

Mono-N-trimethylsilylation of an arylamine such as aniline produces a bathocromic shift of *both* the primary and secondary bands of the same order found for mono-N-alkylation of aniline.[13] This observation is consistent with ^{15}N nmr experiments[6] where the invariance of $J(^{15}N\text{–}H)$ on silylation has been attributed[4] to competition of both the silicon atom and the benzene ring for the nitrogen lone pair. In this circumstance the inductive electron supply[14] of the silicon atom becomes dominant. Bis(N-trimethylsilylation) of aniline must result in severe steric inhibition of resonance,[13] because the secondary band undergoes a large hypsochromic shift and the extinction coefficients of both transitions are greatly reduced.

The invariance of the absorption (200–202 mμ) of both the linear and cyclic polydimethylsilazanes and the proportionality of the extinction coefficient to the number of Si–N bonds in the molecule indicate there is essentially no delocalization or aromaticity associated with the total Si–N framework. This conclusion is supported by the similarity of the base strengths of the silazanes (Table I), as determined by the shift of the C–D stretching frequency ($\Delta\nu$) of $CDCl_3$-amine mixtures.[3] Delocalization in p_π–d_π systems has been discussed in molecular orbital terms by a number of groups. The identical electronic properties of the silazanes may be attributed to the symmetry of the 3d orbitals which, as in the case of the phosphonitrilics,[16] may lead to isolated allylic type (Si–N–Si) chromophores. Alternatively, the large difference in the Coulombic integrals of nitrogen and silicon, possibly coupled with a small resonance integral, will dictate an essentially localized $(p \rightarrow d)\pi$ bond.[17]

A second method of evaluating transmission through the Si–N bond is to examine the modification of the ultraviolet absorption of polysilanes on nitrogen substitution. For example, n-$Me_7Si_3NH_2$ exhibits a hypsochromic shift while n-$(Me_7Si_3)_2NH$[18] exhibits a bathochromic shift when compared with the unsubstituted trisilane, Me_8Si_3. Thus, although the nitrogen atom is interacting with the ground and/or excited states of the silicon chain there is very little interaction of the two Si_3 units across the nitrogen atom in the secondary amine. The basicity of n-$Me_7Si_3NH_2$ is not significantly different from that of triethylsilylamine (Table I), demonstrating the same order of $(p \rightarrow d)\pi$ delocalization in both compounds.

Electronic absorption spectroscopy promises to be a useful technique for the study of other group IV derivatives in which $(p \rightarrow d)\pi$ bonding is postulated.

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[12] An inherent shortcoming of electronic absorption spectroscopy is this inability to quantitatively assess the relative contributions of the ground and excited states to the shifts in the absorption maxima.

[13] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 410.

[14] Electron-withdrawing groups may also cause a bathochromic shift of the primary band, but their effect on the secondary band is much less significant. For example, N-acetylation of aniline results in a bathochromic shift of the primary band but a hypsochromic shift of the secondary band.[15]

[15] H. E. Ungnade, *J. Am. Chem. Soc.*, **75**, 432 (1953).

[16] M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

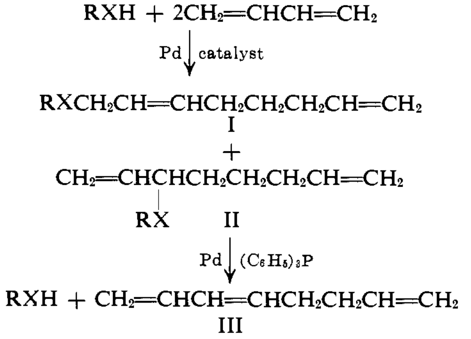
[17] D. P. Craig, *ibid.*, 997 (1959).

[18] Satisfactory elemental analyses and infrared spectra have been obtained for all new compounds described in this communication.

Oligomerization and Dimerization of Butadiene under Homogeneous Catalysis. Reaction with Nucleophiles and the Synthesis of 1,3,7-Octatriene

Sir:

Palladium salts participate in stoichiometric reactions with olefins to form π complexes,[1] with nonconjugated dienes to form σ complexes,[2] and with conjugated dienes to form π-allyl complexes.[3] In solution, palladium salts catalyze the dimerization of olefins.[4] The catalytic activity of supported noble metals, particularly nickel, palladium, and platinum, in hydrogenation and dehydrogenation reactions is equally well known. Previously unknown is a homogeneous reaction between dienes and nucleophiles catalyzed by soluble palladium complexes. We wish to report just such a reaction that involves, in effect, an anti-Markovnikov addition of nucleophiles to a linear butadiene dimer.[5]



$$\begin{array}{c}
\mathrm{RXH + 2CH_2{=}CHCH{=}CH_2}\\
\mathrm{Pd}\downarrow \text{catalyst}\\
\mathrm{RXCH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2}\\
\mathrm{I}\\
+\\
\mathrm{CH_2{=}CH\underset{\underset{RX}{|}}{C}HCH_2CH_2CH_2CH{=}CH_2}\\
\mathrm{II}\\
\mathrm{Pd}\downarrow (\mathrm{C_6H_5})_3\mathrm{P}\\
\mathrm{RXH + CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CH_2}\\
\mathrm{III}
\end{array}$$

Condensation of phenol and butadiene at 60° for 24 hr in the presence of the butadiene–palladium chloride–π–allyl complex[3] leads to a mixture of *o*- and *p*-butenylphenols and phenoxybutene in low conversion (5–10%) and yield (30%). Most solvents are of little effect. However, with pyridine the reaction takes a completely different and unexpected course: 1-phenoxyoctadiene-

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[1] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938); J. N. Dempsey and N. C. Baenziger, *ibid.*, **77**, 4984 (1955); J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

[2] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957); J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Am. Chem. Soc.*, **87**, 3282 (1965); J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966); W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966).

[3] B. L. Shaw, *Chem. Ind.* (London), 1190 (1962); S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); S. D. Robinson and B. L. Shaw, *ibid.*, 5002 (1964); E. J. Smutny, unpublished results.

[4] J. T. van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964); A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967); R. van Helden, C. F. Kohll, and G. Verberg, unpublished results.

[5] Netherlands Patent Application No. 6,606,567 (Nov 15, 1966); E. J. Smutny, U. S. Patent 3,267,169 (Aug 16, 1966).

2,7 was isolated in ~3% yield [bp 85° (1 mm)]. Phenoxyoctadiene absorbs 1.96 moles of hydrogen to give *n*-octyl phenyl ether, which was independently synthesized from sodium phenoxide and *n*-octyl bromide. The double bond positioning at 2 and 7 was clearly indicated from the nmr spectrum [δ 1.5 ppm (2 H), $-CH_2-$; 2.0 (4 H), $=CCH_2-$; 4.3 (2 H), $-OCH_2C=$; 4.9 (2 H), $=CH_2$; 5.6 (3 H), $=CH-$; $\delta \sim 7.0$ (5 H), C_6H_5] from which it was evident that one double bond was terminal and the other allylic to the phenoxy group, but with no methyl groups branched or terminal in the product. The infrared spectrum supports these conclusions (10.1 and 10.95 μ, $-CH=CH_2$; 10.35 μ, *trans*-$CH=CH-$).

Though $(pyr)_2PdCl_2$ was isolated from the reaction mixture and proved to be an active catalyst, no variation of neutral or anionic ligand was superior or raised the conversion of phenol to compound I above 30%. The addition of a stronger base made a profound difference. When phenol (0.4 mole) and butadiene (1.7 moles) were heated at 100° in the presence of palladium chloride (concentrations as low as 5.6×10^{-4} *M*) and sodium phenoxide (1.4×10^{-2} *M*), a 96% conversion of phenol to 1-phenoxyoctadiene-2,7 (I, XR = OC_6H_5, selectivity ~91% *trans*, ~4% *cis*) and 3-phenoxyoctadiene-1,7 (II, XR = OC_6H_5, ~5%) resulted. Phenoxyoctadiene was not obtained from butadiene, phenol, and sodium phenoxide.

There are several remarkable things about this reaction. It is simple, fast, free of significant by-products, and indifferent to the usual poisons. It can be run at elevated temperatures (100 or 150°) under pressure or at reduced temperature (~0°) at atmospheric pressure without change of product, product distribution, or phenol conversion. The reaction can be run with equal success in the presence or absence of solvent (in acetonitrile or chloroform, etc., 100% yield of phenoxyoctadiene). A wide variety of palladium catalysts (*e.g.*, π-allylpalladium chloride or bis(benzonitrile)palladium chloride with sodum phenoxide, etc.) have also been used and proved to be efficient, participating in long catalytic chains. Other metal complexes of group VIII are also effective (*e.g.*, Ru, Pt). The reaction is generally most successful with excess butadiene (phenol:butadiene, 1:4). Other phenols react with butadiene with equal ease (yields 50–100%), giving substituted phenoxyoctadienes (*p*-Cl, *p*-CH_3, *p*-OMe, 2,6-dimethyl, 2,4-dichloro, etc.). Isoprene also participates in the reaction and gives a mixture of phenoxydecadienes.

Related homogeneously catalyzed oligomerizations of butadiene with alcohols, amines, and carboxylic acids have all been realized in excellent yield.[6] The products contain the terminally substituted 8-carbon chain as the predominant isomer.

Butadiene dimerizations in the presence of transition metals to cyclic or branched products are only a recent development.[7] The linear dimerization of butadiene in the presence of a palladium catalyst and a nucleophile also serves as a convenient and easy source of an inaccessible butadiene dimer. Under suitable conditions, phenoxyoctadiene can be converted to 1,3,7-octadiene (III) in good yields and conversions.[5,8] Thus when phenoxyoctadiene was formed at about 0° from phenol (0.106 mole), butadiene (0.42 mole), π-allylpalladium chloride (0.001 mole), and sodium phenoxide (0.0028 mole), and triphenylphosphine (0.0042 mole) was added to the reaction mixture before distillation at reduced pressure, 1,3,7-octatriene (98% pure) was obtained in 85% yield.

Octatriene (bp 122°) is a colorless liquid that slowly polymerized when left in the air unstabilized. The infrared and nmr data [$\delta \sim 2.2$ ppm (4 H), $=CCH_2-$; 4.8–5.3 (4 H), $CH_2=$; 5.4–6.9 (4 H), $=CH-$] confirm the absence of terminal methyl groups and the ultraviolet spectrum [λ_{max} 226 mμ (ϵ 22,700)] and mass spectroscopic fragmentation pattern are consistent with a linear structure with two double bonds conjugated.[9]

The possible mechanism and further extensions of this reaction will be published shortly.[10]

Acknowledgment. The author expresses his thanks to D. W. Wood for experimental assistance.

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[6] E. J. Smutny, T. M. Shryne, and K. C. Dewhirst, unpublished results.

[7] G. Wilke, Belgium Patent 598,363 (1960); S. Otsuka, T. Kikuchi, and T. Taketomi, *J. Am. Chem. Soc.*, **85**, 3709 (1963); T. Saito, Y. Uchida, and A. Misono, *Bull. Chem. Soc., Japan*, **37**, 105 (1964); D. Wittenberg, *Angew. Chem. Intern. Ed. Engl.*, **3**, 153 (1964); T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, 87, 5638 (1965); H. Takahashi, S. Tai, and M. Yamaguchi, *J. Org. Chem.*, **30**, 1661 (1965); H. Muller, D. Wittenberg, H. Seigt, and E. Scharf, *Angew. Chem. Intern. Ed. Engl.*, **4**, 327 (1965); H. Seibt and N. von Kutepow, U. S. Patent 3,277,099 (Oct 4, 1966).

[8] E. J. Smutny and H. Chung, unpublished results.

[9] G. B. Butler and T. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).

[10] NOTE ADDED IN PROOF. S. Takahashi, T. Shibano, and N. Hagihara, [*Tetrahedron Letters*, 2451 (1967)] have reported preliminary results related to ours on the preparation of alkoxyoctadienes and 1,3,7-octatriene.

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Reaction of Tertiary Nitriles with Solvated Electrons

Sir:

In a study of the conversion of dehydroabietonitrile (**1**) to tricyclic steroid analogs[1] of possible physiological activity, numerous routes were explored. It is the purpose of this communication to report on one, which involves the reductive decyanation of dehydroabietonitrile (**1**), to prepare the new compound dehydroabietene ($\Delta^{5,7,14(13)}$-abietatriene,[2] **4**) by solvated electrons in nearly quantitative yield.

Dehydrocyanation[3] of 2,2,3,3-tetraphenylpropionitrile by potassium amide in liquid ammonia by an E2 reaction, as well as decyanation[4] of trisubstituted acetonitriles by sodium amide in boiling aromatic solvents, has been noted. Repeated attempts were made to dehydrocyanate or decyanate **1** by sodium amide in liquid ammonia. In all instances only starting nitrile was recovered. However, interaction of dehydroabietonitrile with the solvated electrons of either sodium biphenyl radical anion or sodium in liquid ammonia afforded high yields of **4** (Scheme I). The products from the reaction of **1** with either one of these reagents

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[2] J. Simonson and D. H. R. Barton, "The Terpenes," Vol. III, University Press, Cambridge, England, 1952, pp 391, 419.

[3] C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 82 (1956).

[4] A. W. Ruddy, *ibid.*, 73, 4096 (1951); M. Jackman, F. C. Nachod, and S. Archer, *ibid.*, 72, 716 (1950); M. Jackman, C. Bolen, F. C. Nachod, B. F. Tullar, and S. Archer, *ibid.*, 71, 2301 (1949).