$= 1{:}4{:}6$;[6] therefore, an initial hypothesis[5] was that the rates in Table I are largely due to steric effects. However, the data do not correlate with E_s but do correlate reasonably well with σ^*. Treatment[7] of the data by eq 2 yields $\rho^* = 11$ and δ (the steric reaction constant) $= 0.6$. A smaller number of rates give $\rho^* = 8$ for the alkaline hydrolysis of $(C_2H_5)_2PO_2R$. These ρ^* values are too large to be explained by rate-determining attack of HO^- to form the pentacoordinate intermediate **2**. Rather, *the breakdown of* the intermediate **2** *to products must be rate determining*.[8] The large ρ^* values can then be understood as a primary effect of the R′ substituents on the value of k_2 since the transition state for k_2 has a partial negative charge on the oxygen atom of the developing alkoxide anion, $R'O^-$. There will also be a secondary effect on the concentration of **2** which will be destabilized by electron donation from R′ relative to the ground state, **1**. Since our hypothesis results in the rate law, $v = k_2[\mathbf{2}]$, these two effects will both contribute.

$$\log (k/k_{CH_3}) = \rho^*\sigma^* + \delta E_s \qquad (2)$$

The hypothesis of rate-determining breakdown of **2** to products is also supported by the following. (1) The relative rates of alkaline hydrolysis of $R_2PO_2CH_3$ (Table II) indicate that both steric and electronic effects are important as expected for substituents at phosphorus. (2) It is useful to examine this system in terms of the chemical dynamics of the intermediate **2** and evaluate the relative energies for loss of RO^- and loss of HO^-. Since alkoxide ions are more basic than hydroxide ion, a higher barrier would be expected for k_2 than k_{-1}.[8] (3) When R′ is an aryl group, then $C_6H_5O^-$ will be a better leaving group than HO^- and the barrier for k_1 and k_{-1} should be the highest point on the energy profile. This change in rate-determining step is in agreement with (a) the much faster rate[9] for $(C_6H_5)_2PO_2C_6H_5$ than for the isopropyl ester (Table I), and (b) $\rho = 2.2$ for $(C_6H_5)_2PO_2C_6H_4X$.[9]

We have not been able to observe any ^{18}O exchange during the alkaline hydrolysis of either $(C_6H_5)_2PO_2R$ or $(C_2H_5)_2PO_2R$ in $^{18}OH_2$ enriched solvents.[5] This indicates that a high-energy pseudorotation of the pentacoordinate intermediate **2** is necessary to put the HO and O^- groups in positions which would allow proton exchange and equivalence. Polarity arguments support **2** as the most likely geometry for the intermediate if trigonal-bipyramidal geometry holds.[1,2]

To summarize, in the alkaline hydrolysis of phosphinates (eq 1) there is evidence for a pentacoordinate intermediate which breaks down to products in the rate-determining step, and the geometry and charge of the pentacoordinate intermediate do not allow ^{18}O exchange between $^{18}OH_2$ and ester.

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[6] E. J. Salmi and R. Leimu, *Suom. Kemistilehti B*, 20, 43 (1947).

[7] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13. We used a modification of eq 2 for analysis of the data: dividing through by σ^* permits a simple graphical analysis of the equation $[\log (k/k_{CH_3})]/\sigma^* = \delta E_s/\sigma^* + \rho^*$.

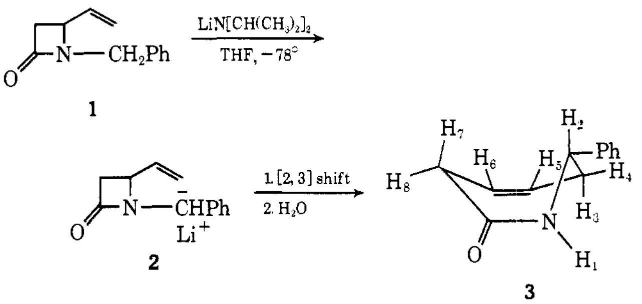
[8] These questions applied to carboxylate derivatives are discussed by W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter 10.

[9] P. Haake, D. R. McCoy, W. Okamura, S. R. Alpha, S. Y. Wong, D. A. Tyssee, J. P. McNeal, and R. D. Cook, *Tetrahedron Lett.*, 5243 (1968).

Base-Induced Ring Enlargements of 1-Benzyl- and 1-Allyl-2-azetidinones

Sir:

As part of a study of the metallation of 1-alkyl- and 1-aryl-2-azetidinones in the 3 position,[1] we attempted the preparation of the 3-lithio derivatives of 1-benzyl-4-vinyl-2-azetidinone (**1**)[2] by reaction of **1** with lithium diisopropylamide in tetrahydrofuran solution at −78°. Instead of the desired result, we obtained in virtually quantitative yield the seven-membered ring unsaturated lactam **3**. The structure of **3** is based on its elemental analysis[2] and spectroscopic properties. The infrared spectrum showed bands at 3420 (N-H) and 1655 cm^{-1} (C=O) while the nmr had peaks at δ 2.4–3.0 (m, $H_3H_4H_8$), 3.5–3.8 (m, H_7), 4.8–5.1 (m, H_2), 4.6–4.75 (m, H_5H_6), 4.8–5.0 (br, H_1), and 7.37 (s, aromatic H).



The transformation **1** → **3** is interpretable in terms of a [2,3] sigmatropic rearrangement of the intermediate benzylic carbanion **2**. A number of such rearrangements involving sulfonium ylides,[3] ammonium ylides,[4] anions α to oxygen,[5] and fluorenyl carbanions[6] have recently been described in considerable detail. The ease with which the above rearrangement occurred is undoubtedly due to relief of ring strain in going from a four- to a seven-membered ring. In agreement with this is the observation that the carbanion from *N*-allyl-*N*-benzylbenzamide did not undergo a [2,3] sigmatropic

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[1] T. Durst and M. J. LeBelle, *Can. J. Chem.*, 50, 3196 (1972).

[2] All 1-alkylated azetidinones were prepared by reaction of the corresponding N–H azetidinone with the appropriate alkyl halide in the presence of powdered KOH (M. J. LeBelle, M.Sc. Thesis, University of Ottawa, 1972). All new compounds reported herein had correct elemental analyses and/or exact molecular weight determinations.

[3] For example: (a) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, 91, 3646 (1969); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *ibid.*, 90, 4758 (1968); (c) B. M. Trost and R. LaRochelle, *Tetrahedron Lett.*, 3327 (1968); (d) G. M. Blackburn, W. D. Ollis, C. Smith, and I. O. Sutherland, *Chem. Commun.*, 99 (1969).

[4] (a) R. W. Jemison and W. D. Ollis, *ibid.*, 294 (1969); (b) G. V. Kaiser, C. W. Ashbrook, and J. E. Baldwin, *J. Amer. Chem. Soc.*, 93, 2342 (1971).

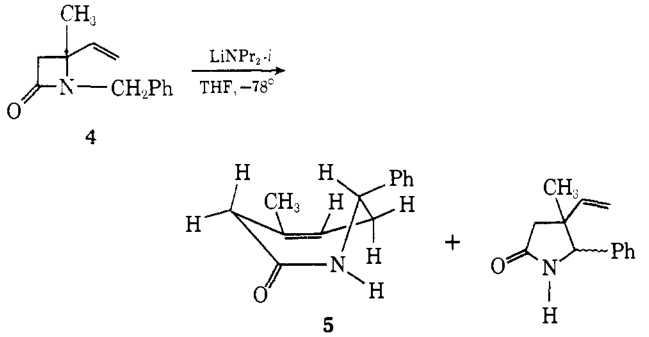
[5] (a) J. E. Baldwin and J. E. Patrick, *ibid.*, 93, 3558 (1971); (b) V. Rautenstrauch, *Chem. Commun.*, 4 (1970).

[6] J. E. Baldwin and F. J. Urban, *ibid.*, 165 (1970).

rearrangement in tetrahydrofuran at room temperature.[7]

The novelty of the rearrangement is that it appears to be the first example of the formation and rearrangement of a carbanion α to an amide nitrogen[8] and secondly, the arrangement of the atoms in the system is such that a ring enlargement by three atoms occurs as a result of the [2,3] shift. The latter concept could conceivably be applied to other [2,3] sigmatropic arrangements and thus be potentially useful for the synthesis of seven-, eight-, and nine-membered rings from the more readily available smaller ring systems.

Reaction of 1-benzyl-4-methyl-4-vinyl-2-azetidinone (**4**) under the above conditions led to the formation of the seven- and five-membered ring lactams **5** and **6** in a 3:2 ratio (total yield 90%). The spectroscopic properties of **5** were entirely analogous to those described for **3**. Compound **6** was obtained as a mixture of isomers which could not be separated by chromatography or fractional crystallization. The nmr spectrum of the mixture showed two sets of singlets at δ 0.74 and 1.37 (ratio 1:3.7, total area 3 H) due to the quaternary methyl groups, and at 4.61 and 4.46 (ratio 1:3.7, total area 1 H) assigned to the benzylic hydrogens. The CH$_2$ group of both isomers had identical chemical shifts in CDCl$_3$ and occurred as an AB quartet, δ_A 2.31, δ_B 2.57 (J_{AB} = 16.5 Hz); in benzene two sets of AB quartets were visible. The remaining vinyl, N–H, and aromatic hydrogen absorptions were as expected. Infrared peaks at 3450, 1700, 1010, and 925 cm^{-1} confirmed the presence of the N–H, C=O, and CH=CH$_2$ groups in **6**. Since a β-methyl group cis to a phenyl ring in a five-membered ring generally absorbs at higher field than if trans,[9] the major isomer of **6** has the methyl and phenyl substituents trans to each other.



4

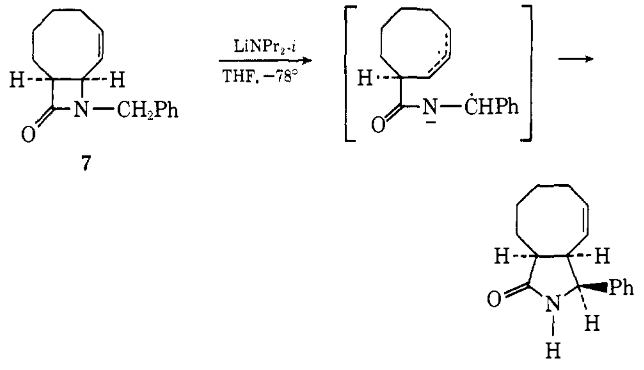
5

6

The formation of **5** and **6** is probably the result of two concurrent processes: (i) a [2,3] sigmatropic rearrangement leading to **5** and (ii) cleavage of the benzylic carbanion to a radical–radical anion intermediate[10] which recombines to give mainly the five-membered ring product **6**. Competition between [2,3] sigmatropic and 1,2 rearrangements is well documented.[3-5,10] In addition Baldwin and coworkers[3a] and Rautenstrauch[5b] have shown that the cleavage–recombination process becomes more important as the temperature is increased. In agreement with this is the observation that the ratio of **5** to **6** decreases from about 1.5:1 to 1:1 as the reaction temperature is raised from −78° to room temperature.

Several earlier examples of 1,2-carbanion rearrangements resulting in a ring expansion by one carbon have been reported.[11] Most closely related to the transformation **4** → **6** is the rearrangement of 1-benzyl-3,3-dimethylazetidine in 18% yield to 2-phenyl-4,4-dimethylpyrrolidine upon refluxing for 24 hr in ether solution.[11a]

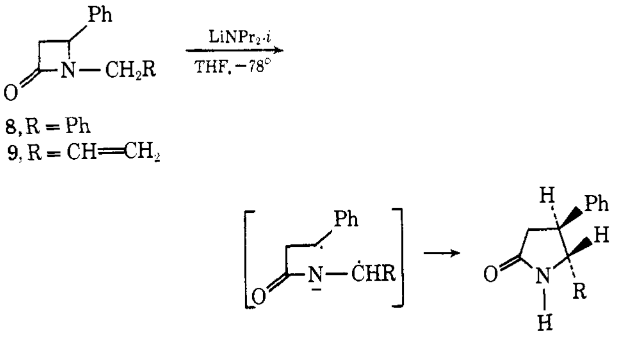
The azetidinones **7–10** were also subjected to the rearrangement conditions. In the case of **7** the restricted position of the double bond does not allow a [2,3] sigmatropic rearrangement and only **11** (92%, ir 3435 and 1695 cm^{-1}), the product of a 1,2 migration, was observed. As in the case of **6**, **11** was obtained as a mixture of isomers, a major one [nmr δ 1.1–3.0 (m, 10 H), 4.37 (d, J = 9.2 Hz, 1 H), 5.5–5.9 (m, 2 H), 6.3 (NH), and 7.30 (s, 5 H)] being tentatively assigned the stereochemistry as shown.



7

11

Rearrangement of **8** and **9** also yielded only the five-membered ring products **12** (93%) and **13** (97%), respectively. The spectroscopic properties and melting points of these products indicated that they were single isomers. These were tentatively assigned the more stable trans configurations mainly on the basis of mechanistic considerations, *i.e.*, closing of the radical–radical anion to give the more stable product. No products resulting from a Sommelet–Hauser type rearrangement were observed.



8, R = Ph
9, R = CH=CH$_2$

12, R = Ph
13, R = CH=CH$_2$

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[7] F. Jung and T. Durst, unpublished observations.

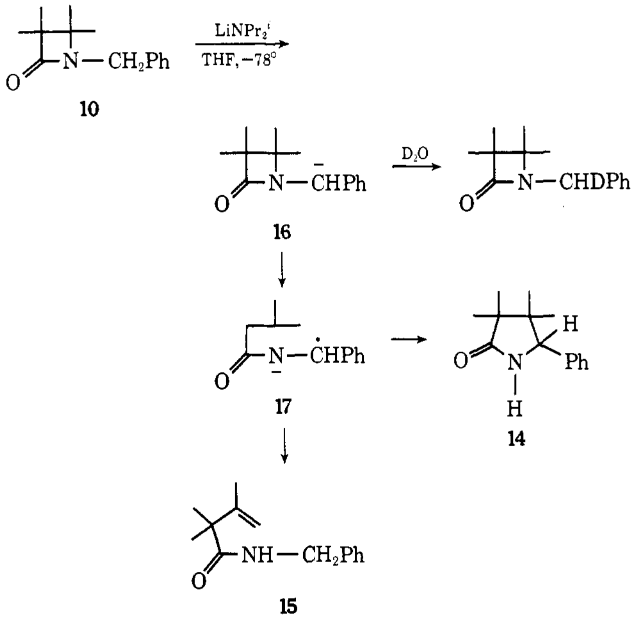
[8] Metallation α to nitrogen in a variety of benzamides and reaction of these derivatives with various electrophiles has recently been achieved: R. R. Fraser, D. Postescu, and J. Whiting, private communication.

[9] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, pp 234–237.

[10] Virtually all 1,2-carbanion rearrangements have been shown to occur *via* cleavage to a radical–radical anion pair, followed by recombination: U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

[11] (a) A. G. Andersen, Jr., and M. T. Wills, *J. Org. Chem.*, **32**, 3241 (1967); **33**, 536, 3046 (1968); (b) H. P. Benecke and J. H. Wikel, *Tetrahedron Lett.*, 289 (1972).

Reaction of **10** with lithium diisopropylamide at −78° for 1 min followed by treatment with D_2O yielded recovered **10** bearing one deuterium in the benzylic position. When the reaction mixture was allowed to warm to room temperature, or when the reaction was carried out at room temperature, the pyrrolidone **14**[12] and the acyclic amide **15**[13] were obtained in 90% yield (approximate ratio 1:1). A rationalization of these results involving the intermediacy of a benzylic carbanion and radical–radical anion **17** is shown below.[14]



Acknowledgment. The financial support of Bristol Laboratories, Syracuse, N. Y., and the National Research Council of Canada is gratefully acknowledged.

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[12] Compound **14** showed the following properties: colorless needles; mp 119–120°; ir ($CHCl_3$) 3435 and 1700 cm^{-1}. The nmr spectrum showed singlets at δ 0.42 (3 H), 0.93 (6 H), 1.08 (3 H) and 4.48 (1 H), and 6.1 (NH), and a multiplet from δ 7.1 to 7.4 (5 H).

[13] Compound **15**, colorless oil, had strong ir bands ($CHCl_3$) at 3435, 1655, 1638, and 903 cm^{-1}; nmr peaks were at δ 1.33 (s, 6 H), 1.73 (br s, 3 H), 4.39 (d, J = 5.0 Hz, 1 H), 4.9–5.0 (m, 2 H), 5.0 (NH), and 7.23 (s, 5 H).

[14] The product **15** could conceivably have arisen from the anion **16** *via* an intramolecular E1cb elimination.

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Dichlorobis(triethylphosphine)nickel(II) as a Catalyst for Reactions of *sym*-Tetramethyldisilane with Unsaturated Hydrocarbons. Novel Synthetic Routes to 1-Silacyclopentadienes and 1,4-Bis(dimethylsilyl)-2-butenes

Sir:

In recent years the hydrosilylation of olefins has been effectively achieved through a process employing a group VIII metal complex as an active homogeneous catalyst. It has been suggested[1] that one of the essential steps in the hydrosilylation process is the oxidative addition of the hydrosilane to the metal complex which originally contains the metal in a low oxidation state. Interestingly, however, none of the reactions of hydrodisilanes, such as pentamethyldisilane and *sym*-tetramethyldisilane, with metal complexes occur without cleavage of the silicon–silicon bond.[2,3] For example, methyldisilicon hydrides disproportionate in the presence of a platinum(II)[4] as indicated by eq 1.

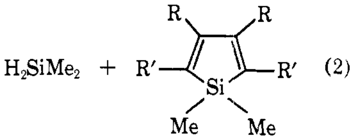
$$\mathrm{RMe_2SiSiMe_2H} \xrightarrow[90^\circ]{\mathrm{PtCl_2(PEt_3)_2}} \Sigma\mathrm{R(Me_2Si)}_n\mathrm{H}\ (n = 1\text{–}6) \qquad (1)$$
$$\mathrm{R = H\ or\ Me}$$

We have suggested there that the reaction most likely involves an α elimination of the methyldisilicon hydride with loss of "dimethylsilylene,"[5] which inserts into the silicon–hydrogen bond present in the original reagent. Evidence for this suggestion has been provided by the fact that the silylene species formed on the platinum catalyst is trapped by diphenylacetylene to give 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (**1**)[7] in low yield (*ca.* 5%).[4b]

We now wish to report that dichlorobis(triethylphosphine)nickel(II) catalyzes the reaction of *sym*-tetramethyldisilane with a variety of disubstituted acetylenes to give 1-silacyclopentadiene derivatives in good yield based on the acetylene used (eq 2).

$$\mathrm{HMe_2SiSiMe_2H} + \mathrm{RC{\equiv}CR'} \xrightarrow[90^\circ]{\mathrm{NiCl_2(PEt_3)_2}}$$

2a, R = R′ = Ph
b, R = Ph; R′ = Me
c, R = R′ = Et
d, R = Bu; R′ = Me



3a, R = R′ = Ph (yield, 56%)
b, R = Ph; R′ = Me (44%)
c, R = R′ = Et (95%)
d, R,R′ = Me or Bu (100%)

Thus, a mixture of *sym*-tetramethyldisilane (2 mmol), diphenylacetylene (2 mmol), and 5 mg of $NiCl_2(PEt_3)_2$ dissolved in 1.5 ml of dry cyclohexane was heated for 18 hr at 90° in a degassed sealed glass tube. On cooling the reaction mixture, green-yellow crystals precipitated. Filtration and washing of the precipitate with a little cyclohexane gave 234 mg (56% yield) of practically pure 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**3a**), mp 178–179° (lit.[8] mp 181–182°).

Similarly, use of 1-phenyl-1-propyne, 3-hexyne, or 2-heptyne gave 1-silacyclopentadiene derivatives (**3b**–**3d**) that are all new and otherwise hardly accessible. Structures have been assigned on the basis of uv and nmr spectra.[9] With 2-heptyne a mixture of three pos-

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[1] A. J. Chalk, *Trans. N. Y. Acad. Sci.*, **32**, 481 (1970).

[2] D. Kummer and J. Furrer, *Z. Naturforsch. B*, **26**, 162 (1971).

[3] A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 3469 (1971).

[4] (a) K. Yamamoto, H. Okinoshima, and M. Kumada, *J. Organometal. Chem.*, **23**, C7 (1970); (b) *ibid.*, **27**, C31 (1971).

[5] The silylene may be by no means a free divalent silicon species,[6] but complexed with platinum.

[6] For pertinent reviews see, *e.g.*, W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

[7] W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968), and references cited therein.

[8] H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964).

[9] For example, **3b**: uv max (cyclohexane) 236 nm (ε 16,000) and 306 (ε 1900); nmr (CCl_4) δ 6.66–7.10 (diffused, 10, Ph), 1.80 (s, 6, Me), and 0.27 ppm (s, 6, Si*Me*). **3c**: uv max (cyclohexane) 300.5 nm (ε 2500); nmr (CCl_4) δ 2.26 (q, 4, J = 7.6 Hz, CH_2Me in α), 2.21 (q, 4, J = 7.6 Hz, CH_2Me in β), 1.03 (t, 6, J = 7.6 Hz, Me in α), 0.98 (t, 6, J = 7.6 Hz, Me in β), and 0.17 ppm (s, 6, Si*Me*).