92%) [^{1}H NMR (CCl_4) δ 2.3–2.0 (m, 2 H), 7.6–5.5 (m, 2 H)]. VPC analysis showed an 8:92 ratio of **4b/5b**.[8]

Thus, it is now possible to convert monosubstituted alkenes to either 2-phenylselenoalkenes **4** or 1-phenylselenoalkenes **5** regioselectively. We are currently developing a variety of synthetic transformations for these substances and will report on them in due course.

References and Notes

(1) Organoselenium Chemistry. 1. This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(2) (a) D. L. Klayman and W. H. H. Gunther, Ed., "Organic Selenium Compounds: Their Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1973; (b) K. B. Sharpless, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, **8A**, 9 (1975), and references cited therein; (c) H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **99**, 263 (1977), and references cited therein.

(3) We have successfully utilized vinyl phenylselenides as synthons for the construction of new carbon to carbon bonds. This work will be reported soon.

(4) (a) Stable seleniranium ions have recently been prepared by the reaction of $ArSePF_6$ with alkenes: G. H. Schmid and D. G. Garrett, *Tetrahedron Lett.*, 3991 (1975). (b) PhSeCl reacts with propene in CH_2Cl_2 to give a 1:1 mixture of i and ii (R = CH_3, X = Cl), and in HOAc to give ii (R = CH_3, X = Cl) exclusively: E. G. Kataev, T. G. Mannafov, E. A. Berdnikov, and O. A. Komarovskaya, *Zh. Org. Khim.*, **9**, 1983 (1973); D. G. Garrett and G. H. Schmid, *J. Org. Chem.*, **42**, 1776 (1977). (c) PhSeOAc reacts with 1-dodecene to give a 1:1 mixture of i and ii (R = n-$C_{10}H_{21}$, X = OAc): K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974). (d) $PhSeOCOCF_3$ gives mixtures of adducts with 1-methylcyclohexene and 1-hexene: H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974); S. Raucher, unpublished results. (e) For studies of the regioselectivity of PhSCl see W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2075 (1968); D. G. Garrett and G. H. Schmid, *J. Org. Chem.*, **42**, 1776 (1977).

$RCH(SePh)CH_2X$ (i) $RCH(X)CH_2SePh$ (ii)

(5) This isomerization presumably involves the reversible formation of the seleniranium ion and the rate is dependent on the leaving group, X. For example, we have observed that for R = n-C_4H_9, i isomerizes to ii in <5 min when X = Br, but requires 24 h when X = Cl (CH_3CN, 25 °C). Also, for R = n-C_4H_9 a 1:1 mixture of i and ii isomerizes to ii in 48 h when X = $OCOCF_3$, but undergoes no apparent change even after 7 days when X = OAc (CH_3CN, 25 °C).

(6) Considerably simpler ^{1}H NMR spectra were obtained for the adducts of 3,3-dimethyl-1-butene and PhSeBr. Kinetic conditions gave exclusively **2h** [NMR (CCl_4): $(CH_3)_3C$– δ 1.15 (s, 9 H); >CHSePh δ 3.30 (dd, J = 6, 12 Hz, 1 H); $-CH_2Br$ δ 3.9–3.6 (m, 2 H)]. Thermodynamic conditions gave exclusively **3h** [NMR (CCl_4): $(CH_3)_3C$– δ 1.05 (s, 3 H); $-CH_2SePh$ δ 3.6–3.1 (m, 2 H); >CHBr δ 4.0 (dd, J = 4, 10 Hz, 1 H)].

(7) This procedure gave better regioselectivity than one which involved the reaction of **1** with PhSeBr in CCl_4 (−20 °C) or $PhCH_3$ (−78 °C), isolation of the β-bromoalkyl phenylselenide, and subsequent dehydrohalogenation (*t*-BuOK, THF, 25 °C).

(8) (a) All compounds were fully characterized by spectroscopic methods. (b) Isolated overall yields from **1** of the vinyl phenylselenide mixtures indicated in Table I were >85% in all instances. (c) VPC analysis was carried out on a Varian 920 using a 5 ft × ¼ in. 1.5% OV 101 on 100/120 Chromosorb G column at 60 mL He/min. In all cases, the retention time of **4** was less than that of **5**. Ratios were determined by triangulation of peaks. (d) A sample of **5b** was prepared by the reaction of $Ph_3P{=}CHSePh$ with pentanal: N. Petragnani, R. Rodrigues, and J. V. Comasseto, *J. Organomet. Chem.*, **114**, 281 (1976); a sample of **4a** was prepared by an alternate procedure which will be detailed shortly: S. Raucher and G. Koolpe, unpublished results.

(9) The rate of disappearance of the dark brown color (THF, −78 °C) is <1 min for **1a–e**, and ~5 min for **1f–l**.

Stanley Raucher

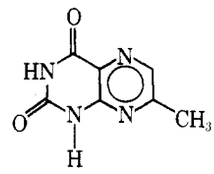
Department of Chemistry, University of Washington
Seattle, Washington 98195

Received June 20, 1977

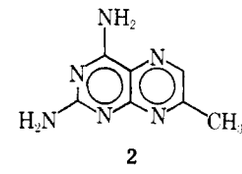
Novel α-Ionization of 7-Methylpteridines. Direct Synthesis of 7-Alkylidenepteridines[1]

Summary: 7-Methylpteridines containing amino or hydroxy groups in the 2,4-positions are converted by aqueous base to carbanions which readily condense with aromatic aldehydes to afford 7-alkylidenepteridines.

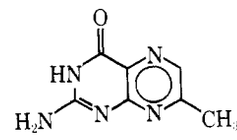
Sir: The carbanion chemistry of parent pteridine systems such as **1–3** which contain an aromatic pyrazine ring appears not to have been explored. In fact, such base-catalyzed chemistry of any pteridines seems limited to the conversion of the N-substituted 3,5,7-trimethylxanthopterin (**4**) to methyl ester **5** using dimethyl oxalate in the presence of potassium methoxide,[2] and to the reaction of N^8-lithio salts of various 2,4-diamino-7,8-dihydropteridines with alkyl halides to afford N^8-alkyl derivatives **6**.[3]



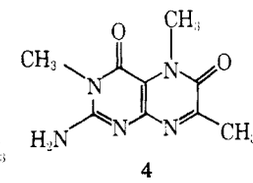
1



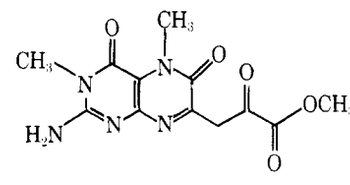
2



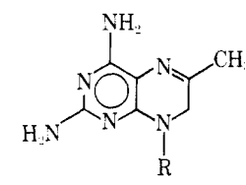
3



4

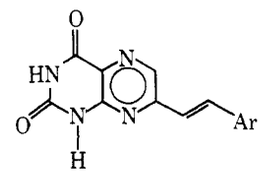


5

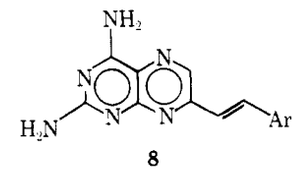


6

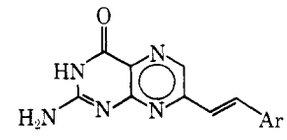
We have found that the methyl groups of 7-methyllumazine (**1**), 2,4-diamino-7-methylpteridine (**2**), and 7-methylpterin (**3**) are conveniently ionized by aqueous/ethanolic sodium hydroxide to afford carbanions α to the aromatic pyrazine rings. Such carbanions readily condense with aromatic aldehydes via the Claisen–Schmidt reaction[4] to give alkylidene derivatives **7**, **8**, and **9**, respectively. Thus, 7-alkylidenelumazines **7**[5] have been derived from **1** and benzaldehyde (53%), *p*-anisaldehyde (27%), 3,4-dimethoxybenzaldehyde (50%), and furfural (39%). Similarly, 7-alkylidene-2,4-diaminopteridines **8**[5] have been obtained from **2** and benzaldehyde (80%), piperonal (73%), and furfural (59%). 7-Methylpterin (**3**) also reacts with such aldehydes; however, the alkylidene derivatives **9** have resisted complete purification thus far since it has not been possible to remove all of the unreacted **3** from the products. As a result, the NMR spectra of these latter products derived from benzaldehyde, *p*-anisaldehyde, and piperonal, though consistent with **9**, contain small absorptions due to **3**.



7



8



9

In a typical experiment, a suspension of 10 mmol of 7-methyllumazine (**1**) and 36 mmol of sodium hydroxide in 20 mL of water is gently warmed until the heterocycle dissolves. The solution is then treated with 15 mmol of benzaldehyde in 10 mL of 95% ethanol and brought to reflux for 2–3 h. Upon

cooling, the precipitated salt of the alkylidene is collected, washed with ethanol and ether, then dried. After acidification with concentrated, boiling hydrochloric acid, the product is collected by filtration and purified by washing with 95% ethanol, then ether. The condensations with **2** are even faster, being essentially complete in 1 h, even though suspensions are present during the entire reaction period. Moreover, pteridines **8** themselves rather than sodium salts are obtained. These products are purified by recrystallization from dimethylformamide.

Though the yields of the alkylidene derivatives have not been maximized, these one-step preparations of **7** and **8** clearly present a viable alternative to earlier 7-alkylidenepteridine syntheses which involved cyclization of appropriate alkylidenepyrazines.[6] Efforts are currently being directed toward the study of various solvent and base combinations in the anticipation of finding ones more compatible with the extremely insoluble pteridines and with electrophiles other than aromatic aldehydes. The application of this methodology to the interesting 6-methylpteridines is also being investigated.

Supplementary Material Available: Full NMR and UV data for compounds **7–8** (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Support of this research by the National Institute of General Medical Sciences, National Institutes of Health, on Grant R01GM21500 is gratefully acknowledged.
(2) W. Pfleiderer, *Chem. Ber.*, **95**, 2195 (1962).
(3) M. Chaykovsky, *J. Org. Chem.*, **40**, 145 (1975).
(4) H. O. House, "Modern Synthetic Reactions", 2nd ed, W.A. Benjamin, Menlo Park, Calif., 1972, pp 632–653.
(5) The structures of these homogeneous compounds (by TLC) were supported by elemental analyses and by IR, UV, and NMR spectroscopy.
(6) E. C. Taylor and T. Kobayashi, *J. Org. Chem.*, **41**, 1299 (1976).

Edwin M. Kaiser,* Stephen L. Hartzell
Department of Chemistry
University of Missouri—Columbia
Columbia, Missouri 65201
Received May 17, 1977