The Barrier to Pyramidal Inversion in Ethylmethylphenylarsine[1]

Sir:

Much of the recent chemistry concerned with pyramidal inversion at second and higher row atoms[2] owes its impetus to a classic study by Weston.[3] A valence force-field calculation utilizing the Costain–Sutherland scheme led him to predict barrier heights for trimethylphosphine (**1**), trimethylarsine (**2**), and trimethylstibine (**3**) of 22.0, 29.2, and 26.7 kcal/mol, respectively.[4] The prediction for **1** was put to the test 10 years later by Horner and Winkler,[5] who reported a barrier of 28–30 kcal/mol for the racemization of methyl-*n*-propylphenylphosphine.[6] However, although evidence for the configurational stability of arsines has not been lacking,[8,9] the uncatalyzed thermal racemization of a monoarsine by the pyramidal inversion mechanism has yet to be reported. We now record the first experimental test of Weston's prediction for **2**, through a study of the thermal racemization of ethylmethylphenylarsine (**4**).

Table I. Racemization of (+)- and (−)-Ethylmethylphenylarsine (**4**) in Decalin at 217.6 ± 0.3°

		Period of observation		Initial specific rotation, deg				
Compd	c, g/100 ml	Sec × 10^{-5}	Days	310 nm	320 nm	330 nm	340 nm	350 nm
(−)-**4**	3.31	12.10	14.00	+38.8	+25.0	+17.2	+12.4	+8.8
(+)-**4**	1.81	11.23	13.00	−27.2	−18.7	−13.0		

The arsine **4**, prepared as previously described,[10] was distilled to yield a sample,[11] bp 42° (0.06 mm), whose pmr spectrum ($CDCl_3$) featured absorptions at δ 7.20–7.62 (m, C_6H_5), 1.15 (s, CH_3As), and 0.89–1.90 (m, CH_2CH_3). Resolution[9] afforded (+)-**4**, $[\alpha]_D$ +0.4 ± 0.1° (*c* 1.81, decalin) and (−)-**4**, $[\alpha]_D$ −0.5 ± 0.1° (*c* 3.31, decalin). Kinetics of racemization at 217.6 ± 0.3° were determined polarimetrically in the 310–350-nm region[12] by the sealed tube method.[13] The racemization was followed over a period of more than 2 half-lives (Table I), and rotations at each wavelength were recorded for five approximately equal time intervals. Satisfactory first-order rate constants were obtained from a least-squares treatment of ln (α_0/α) *vs.* t (Table II). The free energy of activation, $\Delta G^{\ddagger}$, at 217.6°, calculated from the Eyring equation, is 42.4 ± 0.5 kcal/mol.[14]

Compared to a value of 42–46 kcal/mol,[15] Weston's estimated barrier for **2** is too low by approximately the same amount (*ca.* 13 kcal/mol) as his estimated barrier for **1**.

Table II. First-Order Rate Constants for the Thermal Racemization of **4**[a]

	$k^b \times 10^6$, sec^{-1}				
Compd	310 nm	320 nm	330 nm	340 nm	350 nm
(−)-**4**	1.4 (0.998)	1.4 (0.999)	1.4 (0.999)	1.5 (0.998)	1.5 (0.998)
(+)-**4**	1.3 (0.999)	1.2 (0.995)	1.2 (0.991)		

[a] The figures appearing in parentheses below the rate constants are correlation coefficients determined from a least-squares treatment. [b] The estimated error in the rate constants is $\pm 0.4 \times 10^{-6}$ sec^{-1}. The average $k_{rac} = 1.4 \times 10^{-6}$ sec^{-1}, whence $t_{0.5} = 4.95 \times 10^5$ sec or 5.73 days.

Horner and Hofer[16,17] had previously reported that **4** and methyl-*n*-propylphenylarsine show no detectable loss of optical activity on heating for 10 hr at 200°. In light of the present results, these earlier observations are readily accounted for. Assuming $\Delta S^{\ddagger} = 0$ eu, the calculated half-life for the racemization of **4** at 200° is *ca.* 740 hr. Given the low values of $[\alpha]_D$,[8b,9] it may now be appreciated that 10 hr is too short a period of time to allow for the occurrence of significant changes in optical rotation.

On the basis of *photoracemization* studies, Horner and Hofer[16c] had previously concluded that the energy requirement for the *thermal racemization* of tertiary arsines is 59.3–61.0 kcal/mol. That this estimate is grossly at variance with our findings occasions no surprise since photochemical energetics are irrelevant to processes involving only vibrationally excited states of the electronic ground state.

---

(1) This work was supported by the National Science Foundation (GP-30257).

(2) For recent reviews, see A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971).

(3) R. E. Weston, Jr., *J. Amer. Chem. Soc.*, **76**, 2645 (1954).

(4) See also G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *ibid.*, **89**, 3396 (1967) for similar results.

(5) L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964); see also H. D. Munro and L. Horner, *Tetrahedron*, **26**, 4621 (1970).

(6) The only barrier reported for a trialkylphosphine, cyclohexylmethyl-*n*-propylphosphine, is 35.6 kcal/mol.[7] The same study[7] has shown that the barriers in alkylmethylphenylphosphines with alkyl groups as diverse as *n*-propyl, allyl, and *tert*-butyl all fall in the narrow range of 32–33 kcal/mol.

(7) R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970).

(8) (a) I. G. M. Campbell and R. C. Poller, *J. Chem. Soc.*, 1195 (1956); (b) L. Horner and H. Fuchs, *Tetrahedron Lett.*, 203 (1962); (c) K. Mislow, A. Zimmerman, and J. T. Melillo, *J. Amer. Chem. Soc.*, **85**, 594 (1963).

(9) B. Bosnich and S. B. Wild, *ibid.*, **92**, 459 (1970).

(10) G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, 1373 (1920).

(11) *Anal.* Calcd for $C_9H_{13}As$: C, 55.12; H, 6.68; As, 38.20. Found: C, 55.17; H, 7.06; As, 38.32.

(12) All measurements were performed on a Cary 60 spectropolarimeter using a 1-cm cell. Decalin (Aldrich, cis:trans (2:1) distilled from sodium under a dry nitrogen atmosphere) was used as solvent throughout.

(13) All manipulations involving the free arsine were carried out in a drybag under argon. Aliquots of the arsine stock solution were transferred under argon to micro Carius tubes and sealed under vacuum with rigorous exclusion of water and oxygen.

(14) The amount of thermal decomposition at the end of the heating period (over 2 half-lives) never exceeded 13% as determined by glpc and nmr. Neither the rate contants nor the free energy of activation are significantly affected by this process, and the values remain within cited error limits.

(15) By analogy with similar phosphines,[6,7] the barrier to inversion in **4** may be 2–3 kcal/mol lower than that of a trialkylarsine such as **2**.

(16) (a) L. Horner and W. Hofer, *Tetrahedron Lett.*, 3281 (1965); (b) L. Horner and W. Hofer, *ibid.*, 4091 (1965); (c) L. Horner and W. Hofer, *ibid.*, 3323 (1966).

(17) See also L. Horner, *Helv. Chim. Acta*, **49** (Werner Commemoration Vol.), 93 (1967).

G. H. Senkler, Jr., Kurt Mislow*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received November 12, 1971