$$\text{AIBN} \xrightarrow{O_2} RO_2\cdot \quad k_i \qquad (1)$$

$$RO_2\cdot + RH \xrightarrow{O_2} RO_2H + RO_2\cdot \quad k_p \qquad (2)$$

$$RO_2\cdot + R_3N \rightleftharpoons [RO_2^- \cdots {}^+NR_3] \quad K \qquad (3)$$

$$RO_2\cdot + [RO_2^- \cdots {}^+NR_3] \longrightarrow X \quad k_4 \qquad (4)$$

$$2[RO_2^- \cdots {}^+NR_3] \longrightarrow X \quad k_4' \qquad (4')$$

$$[RO_2^- \cdots {}^+NR_3] + RH \xrightarrow{O_2} X + RO_2\cdot \quad k_p' \qquad (5)$$

plex chain termination (4'). This yields the steady-state kinetic expression (6) for the initial inhibited rate, R_i

$$R_i = [RH](k_i[AIBN])^{1/2}\left\{\frac{k_p + Kk_p'[I_n]}{(2Kk_4[I_n] + 2K^2k_4'[I_n]^2)^{1/2}}\right\} \qquad (6)$$

With $k_i = 2.8 \times 10^{-5}$ sec.$^{-1}$ and $k_p = 0.66$ l./mole sec. the solid curve in Fig. 1 was calculated by (6) using $Kk_p' = 574$ l.^{2} mole^{-2} sec.$^{-1}$, $Kk_4 = 3.6 \times 10^6$ l.^{2} mole^{-2} sec.$^{-1}$ and $K^2k_4' = 5.1 \times 10^{11}$ l.^{3} mole^{-3} sec.$^{-1}$ for triethylamine. For tributylamine the parameters are 1.14×10^6, 3.5×10^5 and 8.5×10^{11}, respectively. These values were determined by a line fitting procedure employing a digital computer.

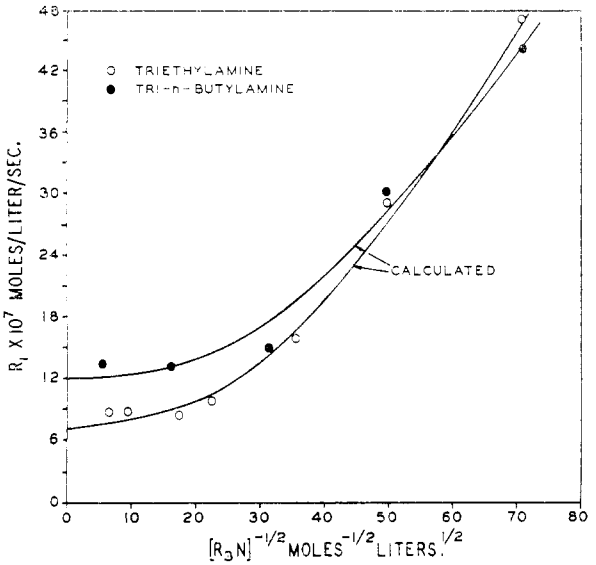


Fig. 1.—Inhibited oxidation rate as a function of trialkylamine concentration: 4 M cumene, 4×10^{-3} M AIBN, 70.0°.

The excellent agreement between observed and calculated values offers support for the mechanism outlined above. It is interesting to compare the value of $Kk_4 = 1.3 \times 10^9$ l.^{2} mole^{-2} sec.$^{-1}$ for diphenylamine under identical conditions[4] with those for trialkylamines. The much higher value for diphenylamines, which follows the simple Boozer and Hammond kinetics, could prevent observation of analogous reactions 4' and 5 of the complex species in this case.

In the preceding article,[5] the quantitative determination of cumylperoxy radical in oxidizing cumene by electron spin resonance is described. With the same technique solutions inhibited by triethylamine and tributylamine at 0.03 M, which is well into the limiting high concentration range, were examined. Under these conditions, no resonance absorption was detectable. The limit of detectability of the $RO_2\cdot$ radical was about $^1/_{20}$ of its uninhibited value, and the limiting oxidation rates are reduced only $^1/_6$ for tributylamine and $^1/_{10}$ for triethylamine from the uninhibited rates. This indicates that the chain is not being propagated by the $RO_2\cdot$ radical but by a second species, namely, the complex, in accordance with the above discussion. Assuming that the e.s.r. line width of the complex is narrow enough to be detected it can be said that K is less than 53 l./mole for triethylamine and 86 l./mole for tributylamine. The previous article sets K for pyridine at 1 or less. It is interesting to note that K for the iodine–triethylamine complex is 880 l./mole at 70° from the data of Nagakura.[6]

The peculiar behavior of trialkylamines as oxidation inhibitors affords additional evidence in favor of the charge-transfer complex mechanism of Boozer and Hammond for oxidation inhibition. It seems clear that the equilibrium constant for formation of complex species between $RO_2\cdot$ radicals and amine-type inhibitors is small. The resulting complexes must, however, engage in very rapid chain termination reactions with $RO_2\cdot$ radicals when an abstractable hydrogen is available as in diphenylamine. A similar, although slower, reaction appears to take place when less available hydrogen is present as in the *n*-alkylamines. It is also interesting to note that $k\rho'$ the propagation rate constant *via* complex, must be greater than 11 and 13 l. mole^{-1} sec.$^{-1}$ for triethyl- and tributylamines, respectively, considerably larger than that for uncomplexed radical. Complexed radical might be expected to react more slowly and more selectively in the manner of chlorine atoms as observed by Russell.[7]

(6) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).
(7) G. A. Russell, *ibid.*, **80**, 4987 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY, NEW YORK 53, N. Y.]

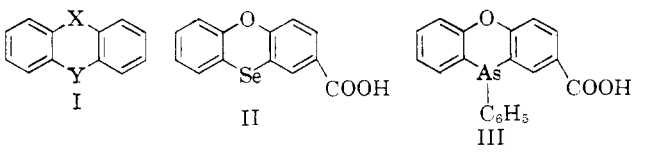
Folded Conformations and Optically Active Triarylarsines[1]

BY KURT MISLOW, ABRAHAM ZIMMERMAN AND JOSEPH T. MELILLO

RECEIVED AUGUST 6, 1962

Homo- and heterocyclic 9,10-dihydroanthracenes (I) exist in folded or "butterfly" conformations. The question of conformational stability is discussed, and it is argued that the reported stereoisomerism in phenoxarsines and in 5,10-dihydroarsanthrenes is best ascribed to the optical stability of the arsenic pyramid. The preparation of an optically active acyclic triarylarsine (VI) and of an optically active 5,10-dihydroarsacridine (IX) lends strong support to these arguments.

It has been pointed out[2] that molecules of type I (XCC = YCC = 120°) cannot be coplanar unless CXC = CYC = 120°. Such molecules are folded about the XY-axis and give rise to folded conformations (butterfly conformations).



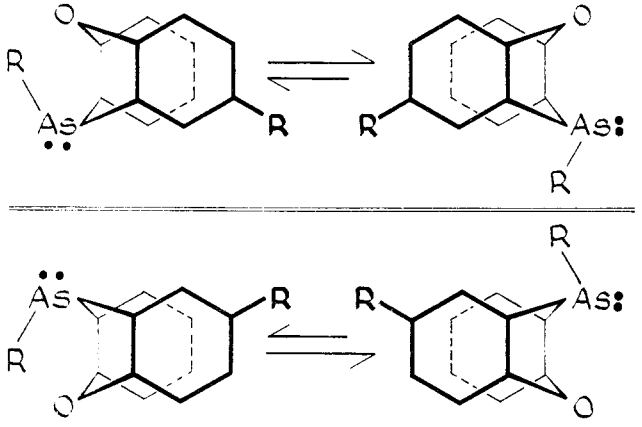
I II III

(1) Grant support by the National Science Foundation (No. G-9205) and by the Alfred P. Sloan Foundation is gratefully acknowledged.

(2) *E.g.*, I. G. M. Campbell, C. G. Le Fèvre, R. J. W. Le Fèvre and E. E. Turner, *J. Chem. Soc.*, 404 (1938); N. J. Leonard and L. E. Sutton, *J. Am. Chem. Soc.*, **70**, 1564 (1948), and references cited therein.

A potential barrier separates a folded molecule and its inverted form. In suitable ring-substituted systems (*e.g.*, II) the two conformers are dissymmetric and the interconversion process is one of racemization. Attempts to achieve resolution of such folded conformers have uniformly met with failure, and it has been recognized that this negative evidence at least *suggests* the rapid interconversion of the flexible enantiomers.[3] The same argument has been used to account for the stereoisomer number in thianthrene sulfoxides.[4]

On the other hand, the successful resolution of several ring-substituted phenoxarsines (I, X = O, Y = AsR, *e.g.*, III) by Lesslie and Turner[5] led these authors to propose that in this particular class of substances the conformational rigidity of the folded molecule is sufficient to give rise to the observed optical stability. The molecules however also contain an asymmetric arsenic atom ($AsR_1R_2R_3$), and in an alternative view the above observations are just as satisfactorily interpreted by invoking the configurational[6] stability of the arsenic pyramid; experimental results obtained by Campbell[7] and theoretical views of Weston[8] now make it appear more than likely that tricoördinate arsenic is configurationally stable (in the sense that the potential barrier to inversion is well above 20 kcal./mole). We are therefore convinced that the resolvable phenoxarsines are most correctly pictured (see accompanying sketch) as separable configurationally stable[6] enantiomers which individually exist in solution as mixtures of rapidly interconverting (flexible) *diastereomeric folded conformations*.[6] It may even be argued that present experimental evidence does not rule out the possibility of a stable planar conformation for these and similar molecules in solution; the erstwhile transition state of stereomutation then would correspond to the stable ground state.



Notwithstanding the weight of evidence to the contrary, Mann[9] has recently maintained that the isolation of two stereoisomeric 5,10-bis-*p*-tolyl-5,10-dihydroarsanthrenes (I, X = Y = $AsC_6H_4CH_3(p)$),[10a] as well as the optical activity of the phenoxarsines, is compatible with the stably folded conformation.[10b] The present work was undertaken in order to provide a forum for further discussion of this persistent issue.

Let us *assume* that the arsenic pyramid is stable in all conformations of I. It is possible to estimate the total valence angle deformation suffered by I (X = Y = AsR) in going from folded ground state to planar transition state (the two R-groups project on the same (*cis*) or on opposite (*trans*) sides of the plane). For the ground state we assume bond angles CCAs = 120° and CAsC = 96°,[11] from which the dihedral angle of fold is calculated to be 118°. In the transition state (dihedral angle 180°), the bond angles will take on values consonant with minimum strain. The bending constants for CCC and CAsC happen to be nearly the same,[12] and if torsional and non-bonded strain are neglected, the computed potential barrier is only 6–7 kcal./mole.[13] Models show that the non-bonded interaction of substituents R is *relieved* in going from ground to transition state; this factor therefore contributes to the *lowering* of the potential barrier. Hence, it seems inconceivable that 5,10-dihydroarsanthrenes and similar molecules are stably folded (if indeed they are folded at all; *vide supra*) though we grant that special factors (such as very large 5,10-substituents) may lead to a situation where one of the two diastereomeric "*exo*" and "*endo*" isomers of the *cis* form exists as by far the most populous component in the mobile conformational equilibrium.

The assumption of pyramidal stability has now been further buttressed by the resolution of an acyclic[14] triarylarsine (VI) and of a compound (IX) containing the 5,10-dihydroarsacridine ring system. The syntheses of VI and IX are outlined in the chart; both compounds were resolved *via* their amphetamine and α-phenylethylamine salts and proved to be optically stable. The resolution of IX substantiates the presumption that the oxygen atom in phenoxarsines does not provide a special function in the process of optical activation. The resolution of VI, which is also the first reported resolution of an acyclic[14] triarylarsine,[15]

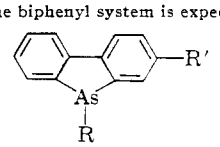
(3) G. M. Bennett, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 444 (1937); G. H. Keats, *ibid.*, 1592 (1937); M. C. Thompson and E. E. Turner, *ibid.*, 29 (1938); I. G. M. Campbell and E. E. Turner, *ibid.*, 37 (1938). However, the troublesome problem of negative evidence[15] remains.

(4) H. Baw, G. M. Bennett and P. Dearns, *ibid.*, 680 (1934).

(5) M. S. Lesslie and E. E. Turner, *ibid.*, 1170 (1934); 1268 (1935); 730 (1936); M. S. Lesslie, *ibid.*, 1001 (1938); 1183 (1949).

(6) For convenience in discussion, we shall adhere to a somewhat artificial distinction between the *conformation* of the folded molecule and the *configuration* of the arsenic pyramid. In principle both isomers may undergo conformational inversion: the butterfly conformation by fluttering and the pyramidal conformation by reversing umbrella.

(7) (a) I. G. M. Campbell, *J. Chem. Soc.*, 1976 (1956); (b) I. G. M. Campbell and R. C. Poller, *ibid.*, 1195 (1956). These authors resolved 9-arsafluorenes (formula). The biphenyl system is expected to be planar.



R = C_6H_5 or C_6H_4COOH
R′ = NH_2 or OCH_3

(8) R. E. Weston, Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954), has calculated a half-life of 2 hours for the pyramidal inversion of trimethylarsine at 107°.

(9) F. G. Mann, in W. Klyne and P. B. D. de la Mare, "Progress in Stereochemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1958, p. 202.

(10) (a) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1184 (1940). (b) After this work was completed, the separation of 9,10-diethyl-9,10-dihydrophosphanthrene into two isomers was reported by M. Davis and F. G. Mann, *Chem. Ind.* (London), 1539 (1962). These authors reiterate earlier views[10a] in their claim that "this isomerism arises from the intervalency angle (97–100°) of the trivalent phosphorus atoms causing the molecule to be folded about the P–P axis, thus giving two alternative relative positions for the ethyl groups. This type of isomerism has been detected in the arsanthrene series." In our view these results serve merely to confirm the demonstrated stability of the phosphine pyramid (*vide infra*[15]).

(11) From the value for trimethylarsine (H. D. Springall and L. O. Brockway, *J. Am. Chem. Soc.*, **60**, 996 (1938)).

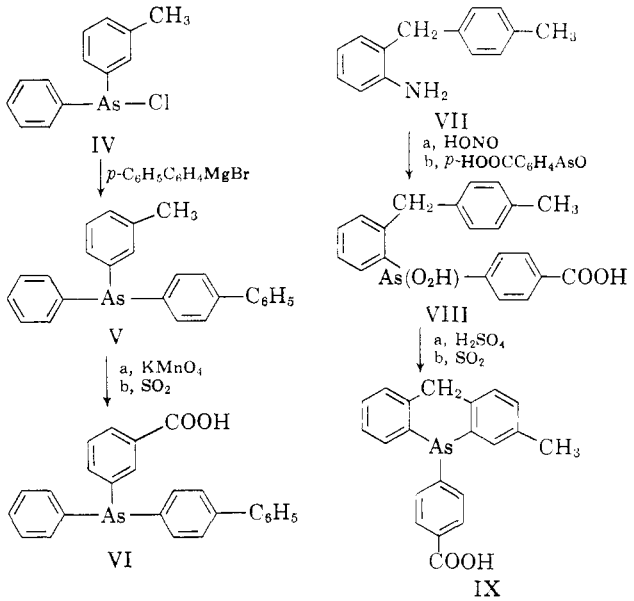
(12) For CCC: 0.8×10^{-11} erg. rad.$^{-2}$ molec.$^{-1}$ (F. H. Westheimer, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12); for CAsC: 0.77×10^{-11} erg. rad.$^{-2}$ molec.$^{-1}$ (from the data for trimethylarsine given by Weston[8]).

(13) In the related 9,10-dihydroanthracene (I, X = Y = CH_2) the calculated barrier is *ca.* 1 kcal./mole (F. H. Herbstein, *J. Chem. Soc.*, 2292 (1959)). Calculations by this author suggest a *stable planar conformation* for 9,10-dihydro-1,2,5,6-dibenzanthracene. For thianthrene (X = Y = S) our estimate of the barrier is 3–4 kcal./mole, taking 106° as the CSC angle[2] and 0.98×10^{-11} erg. rad.$^{-2}$ molec.$^{-1}$ as the CSC bending constant (*cf.* H. Siebert, *Z. anorg. allgem. Chem.*, **271**, 65 (1952)). The previous estimate of 7 kcal./mole by Keats[2] appears to be too high.

(14) Defined as $MR_1R_2R_3$ where M is not part of a ring system.

(15) When this work was completed, a preliminary report appeared of

supplies clinching evidence for the configurational stability of the arsenic pyramid[16] and lends credence to our contention that *the folded conformation in I is highly flexible* and that *the conformational equilibrium is mobile under ordinary conditions.*



Our interest in the optical rotatory dispersion of aromatic systems[17] led incidentally to an examination of the optical rotatory properties of compounds VI and IX. Although the rotation of the cyclic arsine IX, $[\alpha]_D$ −65 and +62° (dioxane), appears to be significantly larger than that of the acyclic compound VI, $[\alpha]_D$ −6 and +4° (dioxane), a comparison of the O.R.D. curves is vitiated: (a) by the uncertainty regarding the optical purity of these substances, (b) by the character (plain) of the curves and (c) by the ambiguity engendered in attempts to assign *comparable* optically active electronic transitions to the two compounds. Here as elsewhere[17] we take the position that significance can be attached to comparative O.R.D. studies only when an analysis of the relevant absorption spectra provides a common and stereochemically meaningful point of reference. Although we are thus constrained at present to forego an evaluation of the O.R.D. data in terms of the relative configuration of VI and IX, it is our intention to continue studies concerned with the optical rotatory properties of compounds in this class.

Experimental[18]

Phenyl-*m*-tolylchloroarsine (IV).—Dry chlorine gas was rapidly passed through a solution of phenyl-*m*-tolylmethylarsine[19] (18.4 g.) in 10 ml. of carbon tetrachloride for 20 minutes. The solvent was removed and the residual phenyl-*m*-tolylmethyldichloroarsine, a viscous liquid, was heated for 1 hour at 140–170° under vacuum (3–25 mm.). The residual oil was fractionally distilled through a 9-inch Vigreux column to give 16.8 g. (85%) of a colorless liquid, b.p. 141° (1–2 mm.), $n^{22}D$ 1.6385.

Anal. Calcd. for $C_{13}H_{10}AsCl$: C, 56.04; H, 4.34; As, 26.39; Cl, 12.73. Found: C, 56.24; H, 4.52; As, 26.76; Cl, 12.51.

Phenyl-*m*-tolyl-*p*-biphenylylarsine (V).—A solution of phenyl-*m*-tolylchloroarsine (IV, 4.15 g.) in 25 ml. of ether was added, over a period of 15 minutes, to a solution of *p*-biphenylylmagnesium bromide prepared from 4-bromobiphenyl (4.66 g.) and 0.48 g. of magnesium in 35 ml. of ether. The mixture was refluxed for 0.5 hour and decomposed with 15% aq. ammonium chloride. The ether layer was washed with aq. ammonium chloride and water, filtered to clarity and stripped to give a residual light orange oil (5.9 g.). A portion (3.5 g.) was chromatographed on silica gel (100–200 mesh). Elution with hexane gave a white solid (1.1 g.), m.p. 73–79°, which was probably a mixture of biphenyl and 4-bromobiphenyl. Continued elution with 5–10% benzene–hexane gave 1.8 g. of a viscous oil (V). On standing for several weeks, crystals slowly formed, m.p. 47–51°.

Anal. Calcd. for $C_{25}H_{21}As$: C, 75.76; H, 5.34; As, 18.90. Found: C, 75.75; H, 5.20; As, 19.04.

(±)-Phenyl-*m*-carboxyphenyl-*p*-biphenylylarsine (VI).—A mixture of crude phenyl-*m*-tolyl-*p*-biphenylylarsine (2.0 g.), potassium permanganate (3.0 g.), sodium hydroxide (1.0 g.) and 40 ml. of water was heated at 95–100° for 2 hours. A considerable precipitate of manganese dioxide had formed and the liquid was almost colorless. Ethanol (0.5 ml.) was added to complete the decolorization. The mixture was filtered, the residue was washed with hot water, and the combined filtrates were acidified with hydrochloric acid to give crude phenyl-*m*-carboxyphenyl-*p*-biphenylylarsine oxide (0.88 g.). Purification was achieved by elution from silica gel with 5–30% ethanol–chloroform or with 5–20% ethanol–ether. The product had an indefinite melting point (formation of a glassy bead at about 125°) and gave an elemental analysis consistent with its formulation as **phenyl-*m*-carboxyphenyl-*p*-biphenylylarsine oxide hydrate.**

Anal. Calcd. for $C_{25}H_{21}O_4As$: C, 65.22; H, 4.60; As, 16.27. Found: C, 65.81; H, 4.70; As, 17.72.

Chromatographed oxide hydrate (8.8 g.) was dissolved in a mixture of 200 ml. of methanol and 200 ml. of concd. hydrochloric acid. A small amount of insoluble reddish gum was removed and the resulting solution was mixed with a solution of sodium sulfite (5.5 g.) and of potassium iodide (0.2 g.) in 30 ml. of water. The mixture was allowed to stand at room temperature overnight. The yellow granular precipitate which had formed was removed by filtration, washed with water and dried. The crude solid (6.8 g.) was recrystallized once from aqueous acetic acid, and the resulting product (4.6 g., m.p. 174–183°) was further purified by chromatography on silica gel, using 2% ether–chloroform as eluent. The material thus obtained (m.p. 195–197°) was recrystallized from aqueous ethanol to give the desired product VI, m.p. 197.5–198°.

Anal. Calcd. for $C_{25}H_{19}O_2As$: C, 70.43; H, 4.49; As, 17.57. Found: C, 70.54; H, 4.63; As, 17.61.

(+)-Phenyl-*m*-carboxyphenyl-*p*-biphenylylarsine (VI).—A solution of racemic VI (1.11 g.) and of (−)-α-phenylethylamine (0.35 g.) in 35 ml. of ethanol was kept in the refrigerator for 1 day. The precipitated salt (0.70 g., m.p. 167–182°, $[\alpha]^{26.5}D$ −0.7° (*c* 0.7, methanol)) was recrystallized twice from ethanol to give white crystals of **salt,** m.p. 178–183° (mostly 181–183°), $[\alpha]^{28}D$ +8° (*c* 0.6, methanol).

Anal. Calcd. for $C_{33}H_{30}NO_2As$: C, 72.39; H, 5.52; N, 2.56; As, 13.68. Found: C, 72.70; H, 5.83; N, 2.48; As, 13.77.

A solution of the salt in methanol was decomposed by addition of cold 0.1 *N* sulfuric acid. The precipitated acid was washed with water and dried to give product, m.p. 188–189°, $\lambda_{max}^{dioxane}$ 263 mμ (ε 26,000)[20]; O.R.D. (*c* 2.0, dioxane, 31°): $[\phi]_{600}$ +16°, $[\phi]_{320}$ +124°.

Anal. Calcd. for $C_{25}H_{19}O_2As$: C, 70.43; H, 4.49; As, 17.57. Found: C, 70.68; H, 4.57; As, 19 ± 1.

(−)-Phenyl-*m*-carboxyphenyl-*p*-biphenylylarsine (VI).—A solution of racemic VI (0.77 g.) and of (+)-amphetamine (0.27 g.) in 25 ml. of ethanol was heated to boiling and filtered. The clear solution was kept overnight at room temperature. The salt crystallized in small circular clusters, m.p. 182–192°.

studies by L. Horner and H. Fuchs, *Tetrahedron Letters*, **No. 5**, 203 (1962), describing the preparation of optically active acyclic[14] *aryldialkylarsines* by electrolytic reduction of optically active quaternary arsonium salts. Optically active acyclic[14] stibines (I. G. M. Campbell, *J. Chem. Soc.*, 3116 (1955); I. G. M. Campbell and A. W. White, *ibid.*, 1184 (1958)) and optically active acyclic[14] phosphines (L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann and P. Beck, *Tetrahedron Letters*, **No. 5**, 161 (1961)) have also been recently reported. It is instructive to note that the numerous attempts by G. Kamai (*Ber.*, **68**, 960 (1935), and following papers) to resolve acyclic arsines all resulted in failure; this illustrates the danger inherent in conclusions drawn from negative evidence.

(16) The compounds studied by Campbell[7] contain arsenic incorporated in a five-membered ring. The internal angle would be expected to resist bending to a greater extent than the external angles, and the deformations would therefore be most unequally distributed. By contrast, the angle deformations in the acyclic arsine VI, though not identical, are at least expected to be more nearly equal. On the assumption that angle strain follows a simple Hooke's law relationship, the racemization of VII will therefore involve a *lower* potential barrier (other things being equal) and constitute a more critical test of pyramidal stability.

(17) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962), and references cited therein.

(18) Melting points are corrected. Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Optical rotatory dispersion was measured by use of an automatic recording Rudolph spectropolarimeter.

(19) G. Kamai, *Ber.*, **68**, 1893 (1935).

(20) Some triarylarsines have been reported with $\lambda_{max}^{ethanol}$ 245–250 mμ (log ε 4.0–4.2); *cf.* F. G. Mann, I. T. Millar and B. B. Smith, *J. Chem. Soc.*, 1130 (1953); I. G. M. Campbell and R. C. Poller, *Chemistry & Industry*, 1126 (1953).

One recrystallization from ethanol gave 0.30 g. of salt, m.p. 191–196°, $[\alpha]^{23.5}D$ −5° (*c* 0.5, methanol), and a further recrystallization from ethanol gave 0.20 g. of **salt**, m.p. 196–198°, $[\alpha]^{24.5}D$ −7° (*c* 0.5, methanol).

Anal. Calcd. for $C_{34}H_{32}NO_2As$: C, 72.72; H, 5.75; N, 2.50; As, 13.34. Found: C, 72.69; H, 5.97; N, 3.30; As, 14.2 ± 0.7.

A solution of the salt in methanol was decomposed by addition of cold 0.1 *N* sulfuric acid. The precipitated acid was washed with water and dried to give solid, m.p. 185–190°, which was recrystallized from aqueous methanol to give the desired product, m.p. 188–189.5°; O.R.D. (*c* 2.1, dioxane, 26°): $[\phi]_{600}$ −24°, $[\phi]_{320}$ −176°. The infrared spectrum (KBr) of (−)-VI was superimposable on that of (+)-VI and was virtually identical with that of (±)-VI.

Anal. Calcd. for $C_{25}H_{19}O_2As$: C, 70.43; H, 4.49; As, 17.57. Found: C, 70.97; H, 4.55; As, 16.97.

2-Amino-4′-methyldiphenylmethane (VII).—A solution of 2-amino-4′-methylbenzophenone (50.0 g.)[21] in 300 ml. of absolute ethanol was added in one portion to small lumps of sodium metal (30.0 g.). After the vigorous reaction had subsided (5 min.), the mixture was stirred for 0.5 hour and heated under reflux for another 0.5 hour. Water (600 ml.) was slowly added to the light yellow solution, with cooling. A yellow oil separated which rapidly solidified upon seeding. The cream-colored precipitate was collected by filtration, washed with 200 ml. of 25% aqueous ethanol and dried to give 45.5 g. (97%) of the desired amine, m.p. 64–65° (lit.[22] m.p. 66°, 65% yield. The earlier procedure[22] called for *amyl* alcohol and a different workup.)

4-Carboxy-2′-(*p*-tolylmethyl)-diphenylarsinic Acid (VIII).—Solution A was prepared as follows: A solution of isoamyl nitrite (2.45 g.) in 15 ml. of ethanol was added over a period of 2 minutes to a cold (−15°) solution of 2-amino-4′-methyldiphenylmethane (VII, 3.43 g.) in 34 ml. of ethanol, to which had been previously added 7 ml. of ethanol saturated with hydrogen chloride. Solution B consisted of *p*-carboxyphenyldichloroarsine (5.15 g., m.p. 156–159°, lit.[7b] m.p. 156–162°) dissolved in 50 ml. of ethanol containing 0.4 g. of suspended copper bronze.

Solution A at −15° was added over a period of 15 minutes to solution B which was maintained at 60°. Nitrogen was evolved during the addition. The ethanol was removed by vacuum distillation and the residual dark green oil was heated at 45–70° with 25 ml. of 4 *N* sodium hydroxide for 15 minutes. The mixture was extracted with ether, the aqueous layer was filtered through Supercel and the filtrate was brought to *p*H 8 by addition of dil. hydrochloric acid. The resulting gummy solid was removed by filtration and the filtrate was acidified to congo red. The resulting finely divided precipitate was collected by filtration, washed with water and dried to yield 5.7 g. (78%) of crude product, m.p. *ca.* 210° dec. Reprecipitation from 2.5% sodium bicarbonate solution followed by recrystallization from aqueous acetic acid afforded the desired arsinic acid, m.p. 214–218° dec.

Anal. Calcd. for $C_{21}H_{19}O_4As$: C, 61.47; H, 4.67; As, 18.26. Found: C, 61.23; H, 4.33; As, 18.43.

(±)-2-Methyl-10-(*p*-carboxyphenyl)-5,10-dihydroarsacridine (IX).—A solution of arsinic acid VIII (5.0 g.) in 20 ml. of concd. sulfuric acid was heated for 6 minutes at 145–152°. The resulting dark brown solution was cooled and slowly added to 450 ml. of cold water. The resulting tan precipitate was collected by filtration, washed with water and dried to give 2.5 g. of crude **2-methyl-10-(*p*-carboxyphenyl)-5,10-dihydroarsacridine-10-oxide.** A solution of 20.0 g. of this oxide in 200 ml. of concd. hydrochloric acid was mixed with (a) a solution of 1 g. of potassium iodide in 1 ml. of water and (b) a solution of 10 g. of sodium sulfite in 50 ml. of water. A brown solid precipitated immediately. The mixture was allowed to stand overnight, and an additional 10 g. of sodium sulfite in 50 ml. of water was added, with stirring. After 10 hours the reaction mixture was filtered and the residue was washed with water and dried to give 19.0 g. of crude product, m.p. 155–160°. Recrystallization from aqueous ethanol afforded the desired arsine, m.p. 187–190°.

Anal. Calcd. for $C_{21}H_{17}O_2As$: C, 67.03; H, 4.56; As, 19.91. Found: C, 67.23; H, 4.58; As, 19.79.

(−)-2-Methyl-10-(*p*-carboxymethyl)-5,10-dihydroarsacridine (IX).—A solution of racemic IX (10.0 g.) and of (+)-amphetamine (3.75 g.) in 350 ml. of ethanol deposited 7.2 g. of a crystalline solid (rosettes) on standing at room temperature overnight. This material (m.p. 209–214°, $[\alpha]^{25}D$ −21° (*c* 0.6, methanol)) was recrystallized four times to give **salt**, m.p. 218–221°, $[\alpha]^{25.5}D$ −58° (*c* 0.5, methanol).

Anal. Calcd. for $C_{30}H_{30}NO_2As$: C, 70.45; H, 5.91; N, 2.74; As, 14.65. Found: C, 70.72; H, 6.10; N, 3.04; As, 14.89.

A solution of the salt in methanol was decomposed by addition of cold 0.1 *N* sulfuric acid. The precipitated acid was washed with water, dried and recrystallized from aqueous methanol to give (−)-IX, m.p. 167–168°, $[\alpha]^{25.5}D$ −83.9° (*c* 0.8, methanol); O.R.D. (*c* 0.55, dioxane, 25.5°): $[\phi]_{600}$ −238°, $[\phi]_{310}$ −2175°.

Anal. Calcd. for $C_{21}H_{17}O_2As$: C, 67.03; H, 4.56; As, 19.91. Found: C, 67.15; H, 4.80; As, 19.85.

(+)-2-Methyl-10-(*p*-carboxymethyl)-5,10-dihydroarsacridine (IX).—The mother liquors from the precipitation of the amphetamine salt (previous section) were concentrated to 150 ml. and refrigerated for 5 days. The precipitate of salt (4.0 g., $[\alpha]^{27}D$ +32° (*c* 0.9, methanol), was removed by filtration and the filtrate was evaporated to dryness. Decomposition of this residual salt with 0.1 *N* sulfuric acid afforded IX, $[\alpha]^{23}D$ +58° (*c* 0.6, methanol).

A mixture of IX (0.60 g., $[\alpha]^{23}D$ +58°), (−)-α-phenylethylamine (0.23 g.) and 12 ml. of ethanol was briefly brought to a boil, allowed to stand for 15 minutes at room temperature, and filtered. The residual solid (0.44 g., m.p. 187–199°, $[\alpha]^{23.5}D$ +59° (*c* 0.6, methanol)) was recrystallized from ethanol to give 0.32 g. of **salt**, m.p. 194–201° (mostly 198–200°), $[\alpha]^{24.5}D$ +61° (*c* 0.6, methanol).

Anal. Calcd. for $C_{29}H_{28}NO_2As$: C, 70.02; H, 5.67; N, 2.82; As, 15.06. Found: C, 70.52; H, 5.88; N, 3.45; As, 16.30.

A solution of the salt in methanol was decomposed by addition of cold 0.1 *N* sulfuric acid. The precipitated acid was washed with water, dried and recrystallized from aqueous ethanol to afford product, m.p. 167–168°, $[\alpha]^{25}D$ +84.1° (*c* 0.7, methanol); $\lambda_{max}^{dioxane}$ 236 mμ (ε 25,000), 278 mμ (shoulder, ε 12,300)[20]; O.R.D. (*c* 0.54, dioxane, 23°): $[\phi]_{600}$ +219°, $[\phi]_{310}$ +2150°. The infrared spectrum (KBr) of (+)-IX was superimposable on that of (−)-IX and was virtually identical with that of (±)-IX.

Anal. Calcd. for $C_{21}H_{17}O_2As$: C, 67.03; H, 4.56; As, 19.91. Found: C, 67.47; H, 4.70; As, 20.01.

(21) H. J. Scheifele, Jr., and D. F. DeTar, *Org. Syntheses*, **32**, 8 (1952).

(22) C. L. Hewett, L. J. Lermit, H. T. Openshaw, A. R. Todd, A. H. Williams and F. N. Woodward, *J. Chem. Soc.*, 292 (1948).