

THE STEREOSPECIFIC ADDITION OF ORGANOARSENIDES TO ALKYNES.

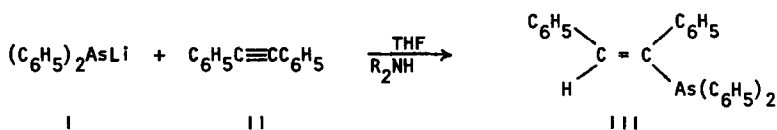
Adam M. Aguiar, Thomas G. Archibald<sup>1</sup>, and Louis A. Kapicak<sup>2</sup>

Chemistry Department, Tulane University  
New Orleans, Louisiana, 70118

(Received in USA 17 June 1967)

Lithium diphenylarsenide (I) (prepared from the alkali metal and triphenylarsine in tetrahydrofuran)<sup>3</sup> has been found to add to both terminal and non-terminal alkynes to give high yields of stereochemically pure vinyl arsines. The stereochemistry of the addition can be controlled by employing the proper amine in the reaction mixture.

Diphenylacetylene (II), in the presence of a secondary amine; e.g., diethylamine, reacts with I in tetrahydrofuran (THF) solution to give cis-1,2-diphenylvinylidiphenylarsine (III), m.p. 105-106° (ethanol) in 62% yield (Eqn. 1).

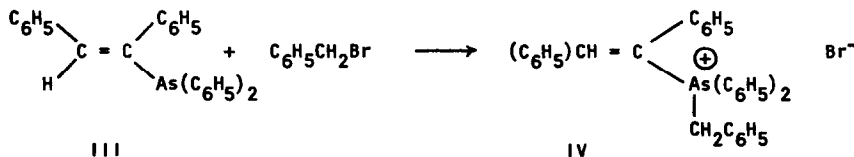


Equation 1.

Elemental analysis calculated for  $\text{C}_{20}\text{H}_{21}\text{As}$ : C, 76.48; H, 5.14; As, 18.36. Found for III: C, 76.20; H, 5.32; As, 18.49.

The proton nmr spectrum of a deuteriochloroform solution of III at 60 MHz, employing an internal standard of tetramethylsilane, exhibited a complex phenyl proton signal centered at  $\tau = 2.7$  ppm and a singlet vinyl proton signal at  $\tau = 3.35$  ppm, whose areas integrated in the ratio of 20:1, respectively.

Reaction of III with excess benzyl bromide in refluxing benzene gave the benzyl arsonium bromide derivative (IV) (m.p. 160-162°) (Eqn. 2).



Equation 2.

Analysis calculated for  $C_{33}H_{29}AsBr$ : C, 68.4; H, 5.0; As, 12.9; Br, 13.8. Found: C, 67.95; H, 5.01; As, 13.36; Br, 14.00.

Presumably, IV has the same stereochemistry as III, but this has not been demonstrated.

The proton nmr of a deuteriochloroform solution of IV showed a phenyl proton complex centered at  $\tau = 2.85$  ppm, another phenyl proton singlet at  $\tau = 2.37$  ppm, the vinyl proton singlet at  $\tau = 2.16$  ppm, and the methylene proton singlet at  $\tau = 4.6$  ppm, whose areas integrated in the ratio of 15:10:1:2, respectively. It is probable that the  $\tau = 2.37$  ppm signal is due to the  $\alpha$ -phenyl group and the phenyl protons on the benzyl group, since the  $\beta$ -phenyl protons and those on the arsenic atom are known to give one complex signal in the  $\beta$ -styryldiphenylarsines.<sup>3</sup> The corresponding phosphonium salt was prepared for proton nmr comparison.

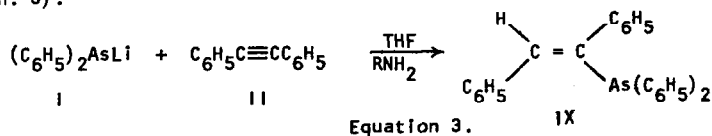
Reaction of cis-1,2-diphenylvinylidiphenylphosphine (V)<sup>4</sup> with excess benzyl bromide in refluxing benzene produced (benzyl)-cis-1,2-diphenylvinylidiphenylphosphonium bromide (VI), m.p. 276-277°, ( $CH_3CN$ ).

The pmr of a deuteriochloroform solution of VI showed the benzyl protons as a sharp doublet centered at  $\tau = 4.75$  ppm ( $J_{PH} = 14$  Hz), two phenyl proton complexes centered at  $\tau = 2.82$  ppm and  $\tau = 2.25$  ppm, and the vinyl proton doublet with the low-field peak at  $\tau = 1.7$  ppm and the up-field peak overlapping with a phenyl complex, but at least 25 Hz away.

Reaction of trans-1,2-diphenylvinylidiphenylphosphine (VII)<sup>4</sup> with excess benzyl bromide in refluxing benzene precipitated (benzyl)-trans-1,2-diphenylvinylidiphenylphosphonium bromide (VIII), m.p. 231-233°, (EtOAc -  $CH_3CN$ ).

The pmr of a deuteriochloroform solution of (VIII) showed the benzyl protons as a doublet centered at  $\tau = 5.68$  ppm ( $J_{PH} = 15$  Hz), the phenyl protons as two complexes centered at  $\tau = 2.85$  ppm and  $\tau = 2.32$  ppm, and the vinyl proton as a doublet centered at  $\tau = 1.65$  ppm ( $J_{PH} = 40$  Hz).

Reaction of a solution of I with II in the presence of a primary amine; e.g., butylamine, gave trans-1,2-diphenylvinylidiphenylarsine (IX), m.p. 128-130° (methanol) in 62% yield (Eqn. 3).



Analysis calculated for  $C_{26}H_{21}As$ : C, 76.50; H, 5.15; As, 18.30. Found: C, 76.32; H, 5.23; As, 18.55.

The nmr spectrum of IX in deuteriochloroform, carbon tetrachloride, methanol- $d^4$ , and dimethylsulfoxide- $d^6$  showed two complex signals centered at  $\tau = 2.75$  ppm, and  $\tau = 3.05$  ppm, whose areas integrated in the ratio of 16:5, respectively.

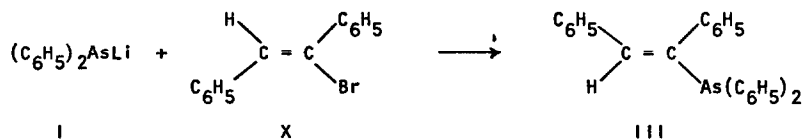
Isomerization of IX to III was accomplished by simply heating it in ethanol solution, or upon a 3% silicon gas chromatographic column heated to  $200^\circ$ . As expected, the  $\beta$ -phenyl group is subjected to less steric hinderance from an  $\alpha$ -phenyl group than from the diphenylarsenic moiety.

Stereochemical assignments to III and IX are also based upon dipole moment measurements. Employing a general radio 1615-A capacitance bridge, Balsbaugh 2TN50 cell, and Bausch and Lomb Modified Abbe-type refractometer, dipole moments of benzene solutions of  $1.25 \times 10^{-3}$  mole fractions of III, IX, and the analogous phosphines, V and VII<sup>4</sup> were taken (Table 1).

TABLE I  
Dipole Moments

Arsines		Phosphines
Cis	(III) $1.370 \pm 0.09$	(V) $1.960 \pm 0.21$
Trans	(IX) $0.970 \pm 0.09$	(VII) $0.990 \pm 0.09$

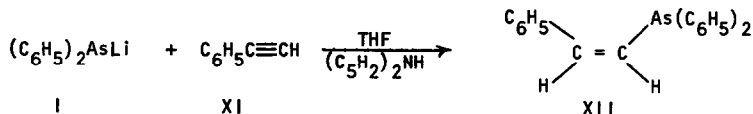
Preparation of III was also accomplished by reaction of I with trans- $\alpha$ -bromostilbene<sup>5</sup> (Eqn. 4).



Equation 4.

In view of the instability of the trans arsine X toward isomerization and the known ability of lithium diphenylarsenide to displace vinyl bromides with retention in configuration,<sup>3</sup> it is likely that X was initially formed and then isomerized to III under the conditions of the reaction. It is also possible that dehydrohalogenation of X to give II occurred and that this was followed by addition of I to give III.

Phenylacetylene (XI) reacts with a THF solution of I in the presence of either primary or secondary amine leading to cis- $\beta$ -styryldiphenylarsine (XII) in 67%, as shown by melting point, as well as mixture melting and proton nmr comparisons with an authentic sample<sup>3</sup> (Eqn. 5).



Equation 5.

Gas chromatographic analysis of the reaction mixture of I and XI alone, at 200°C on a 4' 3% SE-30 silicon column, showed only cis isomer XII. Identical analysis of the same reaction mixture in the presence of either diethylamine or n-butylamine showed 95% X and 5% trans- $\beta$ -styryldiphenylarsine (XIII). Isolated XII and XIII were used as references for this analysis.<sup>3</sup>

These results are in contrast to those obtained in the addition of lithium diphenylphosphide to phenylacetylene in the presence of these amines.<sup>6</sup> In the phosphorus case, the cis isomer is also obtained when a primary or secondary amine is added, but only the trans isomer is obtained in the absence of amines. The explanation may lie in the degree of ionic character present in the lithium-phosphorus and the lithium-arsenic bonds. Whereas the uncomplexed lithium diphenylphosphide has enough covalent character to add in a cis fashion to give the trans-vinylphosphine, uncomplexed lithium diphenylarsenide is ionic enough to add in a trans fashion to give the cis-vinylarsine.

#### REFERENCES

1. N.A.S.A. Fellow, 1965-1967.
2. N.S.F. Undergraduate Research Participant - Summers of 1965 and 1966.
3. A. M. Aguiar and T. G. Archibald, J. Org. Chem., **32**, (in press) (1967).
4. A. M. Aguiar and T. G. Archibald, Tet. Lets., (1966) 5541.
5. S. J. Cristol and W. P. Norris, J. Am. Chem. Soc., **75**, 2645 (1963).
6. A. M. Aguiar and T. G. Archibald, Tet. Lets., (1966) 5471.

#### ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

The dipole moment measurements were made by Mr. John Bullock at Tulane University.