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THE REACTIONS OF TRIPHENYL-PHOSPHINE AND -ARSINE WITH DIMETHYL ACETYLENEDICARBOXYLATE

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Abstract—The phosphine reaction of the title is shown to afford the true pentacovalent phosphole, not a zwitterionic product, but the arsine reaction takes a different course, yielding the acyclic dimethyl triphenylarsenylidene-oxalacetate (VI). Various facets of the chemistry of these systems are reported.

In the course of studies directed toward preparation of heterocycles of the higher fifth-row elements, containing five single bonds to carbon, from the heteroatom, we had occasion to react triphenylphosphine and triphenylarsine with dimethyl acetylenedicarboxylate.[3] The former reaction, independently reported by Johnson and Tebby,[4] yields the unstable yellow adduct, Ia or IIa, the latter formulation being preferred by the English authors. This adduct undergoes a slow spontaneous transformation at room temperature, the major product of which was shown[4] to be III. This transformation, which appears to be accelerated in dilute solution, has made the U.V. spectrum of the adduct unobtainable, but legible N.M.R. spectra could be obtained on very fresh samples. Thus, while the stable transformation product (III) showed four distinguishable ester methoxyl signals ($\tau = 6{\cdot}08$, $6{\cdot}64$, $6{\cdot}67$, $6{\cdot}98$), the cinnamoyl-type phenyl ($\tau = 2{\cdot}44$) and the signals of the other two phenyl groups ($\tau = 2{\cdot}82$, split by coupling with the P^{31} nucleus), samples of the adduct showed only two equal methoxyl singlets at 6·31 and 6·37 and a triphenyl complex, split by phosphorus, centering at 2·70; this spectrum was accompanied by the set of peaks arising from III which increased in intensity with time. The relative, integrated intensities in the two spectra were in accord with their formulations.

That the initial adduct is in fact Ia is shown by the fact that in methanolic acid solution this transformation is far more rapid and quantitative. Protonation of form IIa can only lead to the presumably stable phosphonium salt (IIb), which affords no route for phenyl migration to III, whereas protonation of Ia at any carbonyl oxygen leads to a facile mechanism for 1,2-phenyl migration (IV–V).

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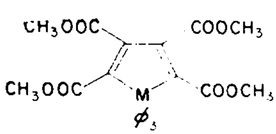
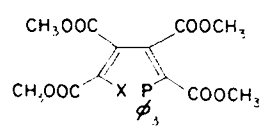
[2] Abstracted in part from the doctoral dissertation of Robert E. Spenger, UCLA, 1962.

[3] Preliminary communication: J. B. Hendrickson, R. E. Spenger and J. J. Sims, *Tetrahedron Letters*, **14**, 477 (1961).

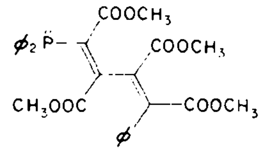
[4] A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 2126 (1961).



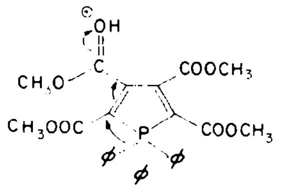
I a, M=P
b, M=As



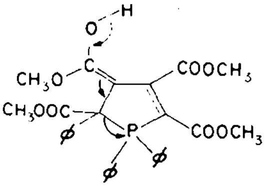
II a, X =
b, X = H



III



IV



V

With this background, when a white crystalline compound with an apparently reasonable analysis was obtained from triphenylarsine and dimethyl acetylenedicarboxylate in ether at room temperature, it was accorded structure Ib;[3] this adduct showed two carbonyl peaks at 5·80 and 6·00 μ similar to those in phosphole Ia. Furthermore, the proton magnetic resonance spectrum of the adduct showed only three sharp peaks ($\tau = 2{\cdot}78$, 6·34, and 6·86). Unlike phosphorus with a nuclear spin of $\frac{1}{2}$, arsenic (nuclear spin $\frac{3}{2}$) does not couple with protons so that the peak at $\tau = 2{\cdot}78$ is a sharp singlet arising from the hydrogens of the three phenyl groups. The U.V. spectrum showed a large peak at 220 mμ and a family of three ($\epsilon \simeq 7000$) at 259 mμ, 264 mμ and 270 mμ very similar to the spectra of triphenylphosphine and arsine oxides[5] and of tetraphenylphosphonium ion[6] but increased in intensity. The latter spectra are said to be little more than that expected from the multiple phenyl absorption and differ notably from spectra of the simple triphenyl compounds (ϕ_3P, ϕ_3As, etc.) in which the unshared electron pair on the trivalent atom can resonate into the phenyl rings.[5]

Evidence for the attachment of the three phenyl groups to arsenic, apart from the mode of formation, was provided by ozonolysis, followed by thiosulfate reduction and sublimation, which yielded authentic triphenylarsine. Similarly, warming with methanolic alkali caused saponification of one ester group to a monoacid which on pyrolysis yielded triphenylarsine oxide as well as triphenylarsine. Diazomethane converted this acid back to the original ester.

Nevertheless, the great thermal stability (sublimes unchanged at 300° *in vacuo*) and lack of color in the triphenylarsine adduct were in such contrast to these properties of the phosphole (Ia) as to cast serious doubts on its formulation as the analogous Ib. While the original analytical values for arsenic were not good, they were also so lacking in self-consistency as virtually to vitiate their usefulness. Later values (see experimental) were more self-consistent.

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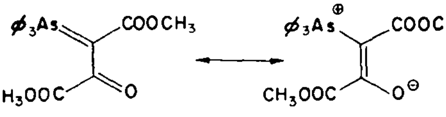
[5] H. H. Jaffee, *J. Chem. Phys.* **22**, 1430 (1954).

[6] J. B. Hendrickson. Unpublished observations.

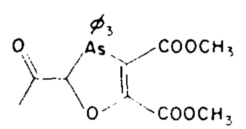
Neutralization equivalents on the mono-acid, however, were self-consistent at a value of 463 ± 4, whereas mono- or di-acids corresponding to IIa require values of 576 and 281, respectively. Two pieces of evidence caused us finally to discard formula Ib for the adduct. Firstly, a strong indication that the "adduct" was in fact in a higher oxidation state was provided by the later recovery of substantial yields of dimethyl fumarate from the reaction of triphenylarsine and dimethyl acetylenedicarboxylate, implying reduction of some of the acetylene ester and concomitant oxidation in the obtained product. Secondly, reaction of the adduct with hydrazine yielded the bishydrazide of oxalic acid.

The foregoing results were in fact well accommodated by structure VI, which may be considered to be a hydrate of a 1:1 adduct with two hydrogens lost. Resonance between the α-arsenylidene ketone and the arsonium enolate zwitterion is indicated by analogy with corresponding triphenylphosphorylidene ketones which have high dipole moments and may be alkylated to give enol ethers.[7] This structure (VI) also accounts for the two different ester groups (one conjugated) which are observed spectroscopically as well as for the larger chemical shift separation of the ester methoxyls in the N.M.R. spectrum from that shown by Ia.[8] The analytical results are in good accord as in the neutralization equivalent of the mono-acid. The correctness of this formulation was subsequently demonstrated by the following experiment. Reaction of the adduct with dry hydrogen chloride in ethlyene chloride at room temperature afforded a high yield of dimethyl oxalacetate as well as triphenylarsine dichloride. Thus, both on stoichiometric and mechanistic grounds, these products dictate VI for the structure of the adduct.

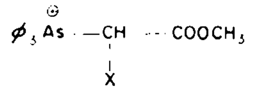


VI

Since there is good precedent[6,7] for O-alkylation of these enolates, it was considered likely that methylation should provide a suitable derivative of VI and that the

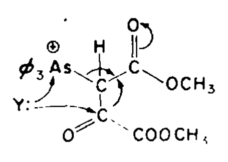


VII

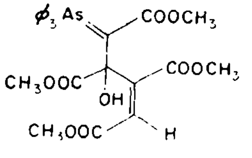


$$\phi_3\overset{\ominus}{As}-\underset{\substack{|\\X}}{CH}-COOCH_3$$

VIII a, X = H
b, X = ⊖



IX



X

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[7] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[8] Whereas the original nuclear magnetic resonance spectrum was obtained on an instrument without machine integration, machine-integrated spectra in fact show a ratio of proton intensities of 5:1:1, as expected for structure VI.

analogous O-phenacyl ether, if it could be induced into a *cis*-orientation, could provide a route to another example of the elusive pentacovalent arsenane heterocycle by the action of base to give VII. Refluxing the arsenane (VI) with methyl iodide in methanol yielded a crystalline iodide salt as shown by precipitation with silver ion and generation of iodine with nitric acid; the salt showed an ester group in the I.R. and afforded triphenylarsine on pyrolysis. However, the product from phenacyl bromide in methanol had an absolutely identical I.R. spectrum and was shown to differ only in being the bromide salt by conversion to the identical iodide on treatment with potassium iodide. Analysis showed these to be salts of VIIIa, which was proved by comparsion with an authentic sample prepared from methyl bromoacetate and triphenylarsine. Thus the other product of the methyl iodide-methanol reaction must have been dimethyl oxalate and this was subsequently isolated from the reaction.

It was found that reaction with the alkyl halides alone or in inert solvents afforded only starting material whereas in methanol alone, even for 48 hours at 100° in a sealed tube, the arsenane (VI) was also largely recovered unchanged. In dilute methanolic HBr, however, the adduct slowly dissolved at room temperature and, on addition of ether, VIIIa precipitated. In general these acid-catalyzed cleavages are readily rationalized by attack of nucleophiles (cf., halide or methanol) on the protonated species IX, either at arsenic or at the ketone position, to cleave the molecule as indicated.

As to the mechanism of formation of VI, it seemed reasonable to postulate the same sequential attack of the triphenylarsine on two molecules of the acetylene as occurs with triphenylphosphine, with the difference that in this case the sequence is

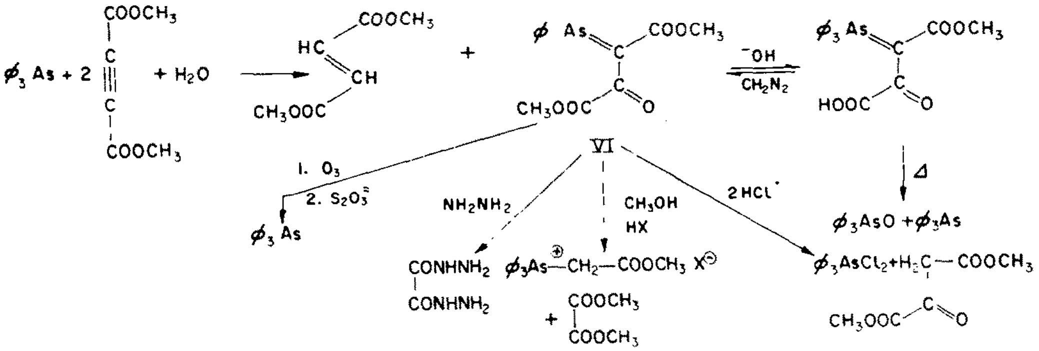

Chart I. Summary of the reactions of the arsenane (VI).

terminated by protonation instead of cyclization. The diene-arsonium cation formed in this way may subsequently add water to form X which can in turn eliminate dimethyl fumarate, yielding VI in a manner similiar to a retroaldol reaction. In support of this view was the result that no reaction occurred under anhydrous conditions and that the presence of water stimulated the otherwise slow and erratic formation of VI. However, the reaction was not stimulated by the addition of weak proton donors (cf., benzoic acid) nor were new adducts formed in the presence of CO_2 or CS_2 as had occurred in the triphenylphosphine series.[4] Finally, the highest yields of VI (77%) and dimethyl fumarate (55%) could be obtained in a far shorter time than was previously the case by warming the reactants on the steam bath for five minutes with a trace of benzoyl peroxide. As this implies a free-radical pathway, the mechanism of the cyclization remains unclear.

Efforts to produce adducts analogous to VI with triphenylantimony and triphenylbismuth have thus far yielded only starting materials.

EXPERIMENTAL[3]

Reaction of triphenylphosphine with dimethyl acetylenedicarboxylate[4]

Equimolar quantities of the reactants were mixed in ether under nitrogen at −50° to afford an immediate yellow precipitate, which was filtered through a sintered glass plate in the side of the flask while still at −50°. Fresh samples decomposed badly to a brown gum in less than 1 hr, but a solution of the fresh adduct in methanol on addition of a drop of methanolic HCl afforded immediate precipitation of yellow crystals of the rearranged product (III) m.p. 255–256° (lit.,[4] 253–255°).

Reactions of triphenylarsine with dimethyl acetylenedicarboxylate

(a) A solution of 20 g (65 mmoles) triphenylarsine and 19 g (130 mmoles) dimethyl acetylenedicarboxylate in 20 ml ether was allowed to stand lightly corked for 10 days. Filtration yielded 2·54 g of white crystals, m.p. 212–214°. The filtrate and ether washings were allowed to stand open for 2 weeks, whereupon the semi-crystalline residue was distilled at 130°/15 mm, affording 2·91 g (30%) dimethyl fumarate, m.p. 102–104°, undepressed with an authentic sample. The residue, on fractional crystallization from methanol, yielded 7·60 g more adduct, m.p. 210–212° (total yield: 10·14 g; 34%), and 7·90 g (40%) recovered triphenylarsine, m.p. 57–60°, undepressed with an authentic sample. I.R. spectra of the dimethyl fumarate and triphenylarsine were also identical with those of authentic samples.

The I.R. spectrum of the adduct showed major bands at 5·80 μ, 6·03 μ, 6·45 μ, 7·8 μ, 8·3 μ and 9·25 μ, the U.V. spectrum at 220 mμ (42,000), 259 mμ (7100), 265 mμ (7300) and 270 mμ (6200), and the N.M.R. spectrum showed sharp singlets at τ-values of 2·78, 6·34, 6·87, intensities 5:1:1, respectively. Samples were recrystallized from methanol to white crystals of m.p. 214°.

	C	H	As
Calc. for Ib, $C_{30}H_{27}AsO_8$:	61·03	4·58	12·79
Calc. for VI, $C_{24}H_{21}AsO_6$:	62·07	4·56	16·13
Found:	61·91	5·92[2]	—
	61·99	4·55[a]	13·72[b]
	62·03	4·94	16·67[b]
	62·61	4·64	15·65[c]
	61·96	4·64	16·36[c]

[a] H. King, UCLA; [b] A. Elek Laboratory, Los Angeles; [c] Schwarzkopf Laboratory, Woodside, N.Y.

(b) Three solutions were prepared, each containing 2·00 ml (2·34 g, 16·4 mmoles) freshly distilled dimethyl acetylenedicarboxylate and 2·52 g (8·2 mmoles) of triphenylarsine in 25 ml solvent, and allowed to stand tightly stoppered for 3 weeks. The first, containing azeotropically dried carbon tetrachloride, yielded no crystals in the medium but 2·4 g recovered triphenylarsine on evaporation and crystallization from methanol. The second, with dry ether as solvent, produced 0·28 g (7%) of adduct VI, m.p. 212–213°, on filtration, while the third, made up with ether and 0·20 ml (11 mmoles) water (which dissolved to one phase in the first several days), yielded 0·67 g (18%) VI, m.p. 212–213°, on filtration.

The carbon tetrachloride experiment was repeated with 24 hr refluxing and with 1 equiv. of added

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[3] We thank Miss Heather King of UCLA for all analyses except those separately annotated. M.p.s were taken on a Fisher m.p. block and are corrected. Spectra were determined on a Perkin-Elmer Infracord (I.R.), Carey 14 spectrophotometer (U.V.), and a Varian A-60 N.M.R. spectrometer; I.R. spectra were determined in chloroform or methylene chloride, U.V. spectra in 95% ethanol and N.M.R. spectra in deuterochloroform.

benzoic acid at room temp for 2 weeks with the same result in each case (95% recovered triphenylarsine). Similar experiments in carbon disulfide or in carbon tetrachloride with slow bubbling of CO_2 over several days also yielded only triphenylarsine, as did similar refluxed solutions.

(c) One milliliter (1·17 g, 8·2 mmoles) dimethyl acetylenedicarboxylate, 1·26 g (4·1 mmoles) triphenylarsine and 0·50 ml (28 mmoles) water were heated on the steam bath several min to melt the solid. Addition of 18 mg (0·07 mmoles) benzoyl peroxide caused a brief sputtering; the mixture was heated 5 more min and, on cooling, congealed to a yellow solid. Trituration with ether and filtration yielded 1·10 g VI, m.p. 210–213°. Evaporation and sublimation of the filtrate afforded 0·30 g(55%) of sublimed dimethyl fumarate, m.p. 104–106°, while the residue, on crystallization from methanol, provided an additional 0·38 g VI, m.p. 208–212°, for a total yield of 1·48 g (77%) of VI.

Ozonolysis of VI

Arsenane (VI; 200 mg) in chloroform was treated with ozone at −20° until effluent ozone appeared (KI-starch color). The solution was then shaken with an aqueous solution of potassium iodide and sodium thiosulfate, dried and evaporated to an oil which afforded on sublimation white crystals of m.p. 52–56°. Recrystallization from methanol yielded 20 mg, m.p. 58–60°, mixed m.p. with authentic triphenylarsine, 58–61°.

Saponification of the adduct (VI)

Compound VI (167 mg) was dissolved in 5 ml 10% potassium hydroxide solution in methanol and refluxed 2 hr. Cooling and pouring into 5 ml 2 N HCl and 15 g ice yielded a white precipitate which was washed with water and dried to yield white crystals m.p. 172–173·5°. The I.R. spectrum (KBr) was very similar to that of the starting ester except for additional broad absorption at 2·8–4·5 μ and a shift of the 5·78 μ peak to 5·90 μ. (Found: C. 61·08; H, 4·24; calc. for $C_{23}H_{19}AsO_5$: C, 61·34; H, 4·26%.)

Treatment of this acid with diazomethane in ether yielded a crystalline product on evaporation; recrystallization from methanol afforded m.p. 212–213°, undepressed with an authentic sample of VI. On vacuum pyrolysis of the acid an oil distilled and crystallized to colorless crystals m.p. 50–60°, undepressed on admixture with authentic triphenylarsine. The I.R. spectra were also identical in these two comparisons. The pyrolysis also produced a sublimed solid, m.p. 180–200°, identified as triphenylarsine oxide by its I.R. spectrum.

A solution of 53·7 mg of the acid in ethanol, titrated to phenolphthalein endpoint, required 1·17 ml 0·100 N NaOH (N.E. 459). A second titration of 164·7 mg required 3·53 ml (N.E. 467). Calc. for $C_{23}H_{19}AsO_5$: 450.

Reaction of VI *with hydrazine*

Adduct VI (0·30 g) and 0·25 ml hydrazine hydrate were refluxed in 2-methoxyethanol for 16 hr. The solid dissolved slowly over the first ½ hr. A crystalline precipitate formed in the hot liquid after 8–10 hr. Cooling and filtration yielded 49 mg of white needles. A sample, purified by micro-soxhlet crystallization with methanol, melted with decomposition in a sealed capillary at 232–235° (lit.[10] for dihydrazide of oxalic acid, 235°). (Found: C, 20·23; H, 5·18; calc. for CH_3N_2O: C, 20·34; H, 5·12%.)

Reaction of VI *with hydrogen chloride*

Dry hydrogen chloride was passed briefly through 10 ml ethylene chloride and 0·23 g VI was then added and allowed to stand 2 days. The solvent, still acidic, was evaporated *in vacuo* to yield 0·25 g of dry solid from which on vacuum pyrolysis at 90°/15 mm were obtained 0·08 g of sublimed crystals, m.p. 74·5–76·5°. (Found: C, 44·98; H, 5·06; calc. for $C_6H_8O_5$: C, 45·00; H, 5·04%).

This product was identified as dimethyl oxalacetate by conversion[11] to the phenylhydrazone, m.p. 115–118°, mixed m.p. 116–119° with a sample prepared from dimethyl acetylenedicarboxylate and phenylhydrazine,[12] m.p. 118–119° (lit,[12] 116–118°.)

The residue from the sublimation consisted of 0·17 g crystalline solid, m.p. 150–200°, undepressed by admixture with authentic triphenylarsine dichloride, m.p. 160–206° (lit.[18] 158–205°), prepared by

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[10] Curtius, Schöfer and Schwan, *J. prakt. Chem.*, **51**, 194 (1895).

[11] W. Wislicenus and A. Grossmann, *Ann.*, **277**, 375 (1894).

[12] E. Buchner, *Ber.*, **22**, 2930 (1889).

passing chlorine into a solution of triphenylarsine.[18] Each sample of dichloride was also converted to the hydroxychloride by shaking a methylene chloride solution with water and evaporating to dryness. The hydroxychlorides melted at 160–172° and 158–166°, respectively (lit.[18] 171°), and did not depress on admixture. Identity in each case was confirmed by I.R. comparisons.

Reaction with methyl iodide in methanol

A solution of 5·1 g VI in 50 ml methanol and 50 ml methyl iodide was refluxed 24 hr and the solvents removed on the steam bath with an air-jet. The semi-crystalline mass was passed through a silica gel column in chloroform, the first fractions yielding a dark oil from which crystals could be sublimed, m.p. 50–55°, undepressed by authentic dimethyl oxalate, which also had an identical I.R. spectrum. Elution of the column with 5% methanol in chloroform afforded 3·3 g (60%) crude VIIIa iodide, recrystallized from isopropanol to m.p. 144–148°, I.R. bands at 5·78 μ (s), 6·20 μ and 6·33 μ (w), N.M.R. peaks at $\tau = 2{\cdot}38$ (15), 4·87 (1·8), and 6·56 (3) (intensities in parentheses). A methanol solution turned brown on addition of nitric acid and gave a blue starch color, addition of silver nitrate solution gave an immediate thick yellow precipitate. (Found: C, 49·89, 49·90; H, 3·98, 4·00; As, 9·86; I, 24·41, 25·51; calc. for $C_{21}H_{20}AsO_2I$: C, 49·86; H, 3·99; As, 14·80; I, 25·07%.)

Refluxing VI 3 days in methyl iodide alone yielded starting material, m.p. 200–210°, quantitatively. Solution of VI in methanol occurred rapidly after brief passage of dry hydrogen bromide into the solution; dilution with ether afforded a precipitate of VIIIa bromide, m.p. 167–168°, undepressed with an authentic sample (below).

Reaction with phenacyl bromide

A solution of 1·00 g (2·2 mmoles) VI and 3·00 g (15 mmoles) phenacyl bromide in 20 ml methanol was refluxed for 20 hr and evaporated *in vacuo* to yield a dark oil which on trituration with ether yielded 0·93 g (97%) crystals, m.p. 166–170°, with an I.R. spectrum identical to that of VIIIa iodide produced above. The mixed m.p. with authentic sample of VIIIa bromide (below) was 166–170°. A solution of 0·20 g of these crystals in methanol was treated with a solution of 0·40 g potassium iodide in 2 ml water. The white precipitate was filtered, yielding 145 mg, m.p. 148°, undepressed by admixture with the crystals of VIIIa iodide from iodide-methanol.

Triphenyl-carbomethoxymethylarsonium bromide (VIIIa)

A solution of 4·0 ml (6·55 g, 43 mmoles) methyl bromoacetate and 13·1 g (43 mmoles) triphenylarsine in methanol was refluxed for 16 hr, allowed to cool and poured into ether to produce an oil which soon crystallized. This was filtered and washed with ether to yield 17·2 g (87%) VIIIa bromide, m.p. 169–170°. This material was used in the identity experiments above. Treated with potassium hydroxide briefly it yielded the arsenane VIIIb in the typical way,[7] m.p. 133–140°, carbonyl band shifted from 5·78 μ in VIIIa to 6·13 μ in the I.R. spectrum, analogous to the behavior of the corresponding phosphorus compound.[6]

[18] A. Michaelis, *Ann.*, **321**, 141 (1902).