J. Chem. Soc. (C), 1971

Some Reactions of Arsenic Ylides

By S. Trippett* and Margaret A. Walker, Department of Chemistry, The University, Leicester LE1 7RH

para-Substituted benzylidenetriarylarsoranes with para-substituted benzaldehydes give olefins when the benzylidene para-substituent is strongly electron attractive otherwise epoxides are formed. Methylenetriphenylarsorane with αβ-unsaturated ketones gives cyclopropanes and benzylidenetriphenylarsorane with Schiff's bases gives aziridines. Reactions of arsoranes with dimethyl acetylenedicarboxylate, phenylsulphine, and phenylsulphene are also described.

THERE have been few reports on the reactions of arsenic ylides with carbonyl compounds since those of Wittig and Johnson showed that in general the betaines (I) formed from arsenic ylides and carbonyl compounds can give either arsine and epoxide or arsine oxide and olefin. Olefin was obtained from methylenetriphenylarsorane and benzophenone¹ (together with triphenylarsine and diphenylacetaldehyde) and from fluorenylidenetriphenylarsone and substituted benzaldehydes,² while both olefin and epoxide were formed from benzylidenetriphenylarsonane and p-nitrobenzaldehyde in ether.³ The stable arsoranes $Ph_3As:CH\cdot COR$ (R = OEt, Me, or Ph) with aldehydes gave olefins.⁴ In order to determine the factors which control the direction of elimination from the betaines (I) we have studied the reactions of substituted benzylidenetriarylarsoranes with parasubstituted benzaldehydes.

The reactions were carried out in ethanolic sodium ethoxide at room temperature and the results are in the Table. In no case were both olefin and epoxide ob-



tained and in all cases only trans-olefin or trans-epoxide was detected. Clearly, the determining factor for

563.
² A. W. Johnson, J. Org. Chem., 1960, 25, 183.
³ A. W. Johnson and J. O. Martin, Chem. and Ind., 1965,

olefin formation is the presence of a grouping R^1 which is able to stabilise an adjacent carbanion, and it is reasonable to suppose that in the transition state (3)

Reactions of $Ar_3 As \cdot CH_2 R^1$ with $p - R^2 C_6 H_4 \cdot CHO$ in EtOH-EtONa at room temp.

				%	%
Expt.	\mathbf{Ar}	R^1	\mathbb{R}^2	Epoxide	Olefin
1	\mathbf{Ph}	\mathbf{Ph}	н	90	
2	Ph	\mathbf{Ph}	Cl	76	
3	Ph	\mathbf{Ph}	OMe	56	
4	\mathbf{Ph}	\mathbf{Ph}	NO_{2}	75	
5	Ph	\mathbf{Ph}	CN^{-}	87	
6	\mathbf{Ph}	p-ClC ₆ H ₄	Н	51	
7	Ph	p-ClC ₆ H ₄	NO_2	86	
8	\mathbf{Ph}	p-NO ₂ ·C ₆ H ₄	н		40
9	\mathbf{Ph}	p-NO ₂ ·C ₆ H ₄	NO_2		96
10	\mathbf{Ph}	p-CN·C ₆ H ₄	н		67
11	\mathbf{Ph}	Ĥ	н	87	
12	\mathbf{Ph}	CO_2Et	Н		77
13	p-MeO·C ₆ H ₄	Ph	NO_2	75	
14	p-MeO·C ₆ H ₄	p-NO ₂ ·C ₆ H ₄	\mathbf{H}		75
15	p-MeO·C ₆ H ₄	p-NO ₂ ·C ₆ H ₄	NO_2		95

for olefin formation from the five-co-ordinate intermediate (2) breaking of the As-C bond is in advance of other electron shifts and the α -carbon bears a fractional negative charge. Stabilisation of this charge leads to faster olefin formation. A similar distribution of charge has been suggested ⁵ in the transition state for olefin formation from phosphonate carbanions.

With phosphorus ylides the use of tris-p-methoxy-

⁴ N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk, 1965, 1474. ⁵ E. J. Corey and G. T. Kwiatkowski, J. Amer. Chem. Soc.,

¹ M. C. Henry and G. Wittig, J. Amer. Chem. Soc., 1960, 82,

^{1968, 88, 5655.}

phenylphosphonium salts so reduces the electropositive character of the phosphorus that elimination of phosphine oxide from the betaines is inhibited.⁶ This was not so with tris-p-methoxyphenylbenzylarsonium salts



(I)

(3) ļi

\|/ As || +

CHR1

Attempts to carry out olefin or epoxide syntheses with allytriphenylarsonium bromide in ethanolic sodium ethoxide gave only 2-ethoxypropyltriphenylarsonium bromide. Under the same conditions no reaction was observed with ethyltriphenylarsonium bromide.

With phosphorus ylides and $\alpha\beta$ -unsaturated ketones products derived from attack of the ylide at the β position are obtained only if the carbonyl group is sterically hindered. Methylenetriphenylarsorane gave the corresponding cyclopropanes (4), from β -attack, with both benzylidene-2',4',6'-trimethylacetophenone and the unhindered benzylideneacetophenone.

In its reactions with Schiff's bases benzylidenetriphenylarsorane resembles sulphur rather than phosphorus ylides in that aziridines are the major products. Thus the arsorane, generated in ether using butyllithium, with benzylideneaniline gave 1,2,3-triphenylaziridine in 50% yield. Attempts to make p-nitrobenzylidenetriphenylarsorane, generated from the salt and ethanolic sodium ethoxide, react with Schiff's bases gave only the products of direct alcoholysis, that is arsine, arsine oxide, p-nitrotoluene, 4,4'-dinitrodibenzyl, and 4,4'-dinitrostilbene. These could be formed as shown in Scheme 1.

Among other reactions of arsenic ylides investigated are those of the stable arsoranes (5; R = OEt, C_6H_4 -

Br- ϕ) with dimethyl acetylenedicarboxylate, to give the arsoranes (6; R = OEt, C_6H_4Br-p) in reactions entirely analogous to those ⁷ of the corresponding phosphoranes, and with phenylsulphene and phenylsulphine. With the arsorane (5; $R = C_6 H_4 Br - p$) phenylsulphine gave the stable arsorane (7; $R = C_6 H_4 Br - p$) formed by proton transfer in the initial adduct, while the arsorane (5;

$$Ph_{3}\dot{A}s:CH_{2}Ar + \bar{O}Et \implies Ph_{3}As(-CH_{2}Ar) \cdot OEt$$

$$Ph_{3}\dot{A}s:CH_{2}Ar + \bar{O}Et \implies Ph_{3}As(-CH_{2}Ar) \cdot OEt$$

$$Ph_{3}\dot{A}s:CH_{4}Ar \qquad Ph_{3}\dot{A}s:OEt + Ar\bar{C}H_{2}$$

$$Eto^{-}$$

$$ArCH_{2}\dot{A}sPh_{3} \qquad Ph_{3}AsO + Et_{2}O$$

$$Ph_{3}\dot{A}s=CH\cdot Ar$$

$$Ph_{3}\dot{A$$

R = OEt) with phenylsulphene⁸ gave ethyl cinnamate, triphenylarsine, and the arsorane (8). Presumably the cinnamate was formed via the trans-episulphone (9).



These reactions of arsenic ylides, when compared with those of the corresponding phosphorus ylides, are consistent with the relative weakness of both the As-C and As=O bonds.

⁸ For the reactions of sulphoxonium ylides with sulphenes see J. Ide and Y. Yura, Tetrahedron Letters, 1968, 3491.

⁶ G. Wittig, H. D. Weigmann, and M. Schlosser, Chem. Ber., 1961, 94, 676. 7 H. J. Bestmann and O. Rothe, Angew. Chem. Internat.

Edn., 1964, 3, 512.

EXPERIMENTAL

Except where stated i.r. spectra were recorded as Nujol mulls and ¹H n.m.r. spectra were recorded for solutions in deuteriochloroform with a Varian A-60 spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument; in each case the molecular ion is given first followed by peaks of structural significance. Light petroleum had b.p. $40-60^{\circ}$.

Reactions of Arsoranes with Benzaldehydes.---The arsonium salt (10 mmole) and the aldehyde (11 mmole) in ethanol (50 ml.) containing sodium (0.23 g.) were set aside at room temperature for 24 hr. G.l.c. on the reaction mixture was then used for the estimation of trans-stilbene epoxide (2 m. Apiezon column at 200°), styrene oxide (same column at 145°), and ethyl cinnamate (same column at 210°). Solvent was then evaporated off and the residue was extracted with chloroform. The extract was washed with water, dried, and evaporated and the residue was chromatographed on basic alumina. Triphenylarsine, epoxide or olefin, and arsine oxide were eluted in that order. Known compounds were identified by their i.r., n.m.r., and mass spectra and by mixed m.p. when possible. The new compounds were 4-chloro-trans-stilbene epoxide, m.p. 101-102° (from ethyl acetate), v_{max} 820 and 845 cm.⁻¹, m/e 230 (³⁵Cl), 214, and 124 (Found: C, 72·4; H, 4·45; Cl, 15.4. C₁₄H₁₁ClO requires C, 72.9; H, 4.8; Cl, 15.4%), 4-chloro-4'-nitro-trans-stilbene epoxide, m.p. 129°, vmax. 850 and 818 cm.⁻¹, m/e 275 (³⁵Cl), 259, 135, and 124 (Found: C, 61·1; H, 3·6; N, 5·1. $C_{14}H_{10}ClNO_3$ requires C, 61·0; H, 3.6; N, 5.1%), and 4-cyano-trans-stilbene epoxide, m.p. 69°, v_{max.} 845 and 825 cm.⁻¹; m/e 221, 205, and 115 (Found: C, 81.5; H, 5.1; N, 6.5. C₁₅H₁₁NO requires C, 81.4; H, 5.0; N, 6.3%).

Reaction of Allyltriphenylarsonium Bromide with Ethanolic Sodium Ethoxide.—The salt (1 g.) in ethanol (50 ml.) containing sodium (0.05 g.) was set aside at room temperature for 8 hr. Solvent was then evaporated off and the residue, in chloroform, was washed with water, dried, and the solvent evaporated off. Crystallisation of the residue from chloroform-ethyl acetate gave 2-ethoxypropyltriphenylarsonium bromide (1 g.), m.p. 203—204°, v_{max} 1147 and 1095 cm.⁻¹, τ 9·2 (3H, t, J 7 Hz), 8·5 (3H, d, J 2·5 Hz), 7·2—7·8 (1H, m), 5·6—6·8 (3H, m), 5·1—5·5 (1H, m), and 2·1—3·3 (15H, m) (Found: C, 58·8; H, 5·45; Br, 17·3. C₂₃H₂₆AsBrO requires C, 58·4; H, 5·5; Br, 16·9%).

Reaction of Methylenetriphenylarsorane with Benzylideneacetophenone.—Methyltriphenylarsonium iodide (6 g.) was stirred with $1\cdot1n$ -butyl-lithium ($12\cdot3$ ml.) in ether (50 ml.) at room temperature for $1\cdot5$ hr. Benzylideneacetophenone ($2\cdot8$ g.) in ether (10 ml.) was then added slowly and the solution was extracted under reflux for 16 hr. after which it was poured into water. The chloroform extract was washed with water, dried, and evaporated; the residue was chromatographed on basic alumina. Elution with light petroleum gave triphenylarsine ($1\cdot9$ g.), m.p. and mixed m.p. 60°. Elution with light petroleum-benzene (1:1) gave 1-benzoyl-2-phenylcyclopropane ($1\cdot5$ g.), m.p. and mixed m.p. 49—50°, having i.r. and n.m.r. spectra identical with those of an authentic sample prepared ⁹ from benzylidene acetophenone and dimethyloxosulphonium methylide.

A similar experiment using benzylidene-2',4',6'-trimethylacetophenone (3.4 g.) gave triphenylarsine (1.5 g.) and

⁹ E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 1965, 87, 1353.

1-mesitoyl-2-phenylcyclopropane (1.6 g.), b.p. 188° at 1 mmHg, having i.r. and n.m.r. spectra identical with those of an authentic sample prepared from benzylidene-2',4',6'-trimethylacetophenone and dimethyloxosulphonium methylide.

Reaction of Benzylidenetriphenylarsorane with Benzylideneaniline.—Benzyltriphenylarsonium bromide (4 g.) was stirred with 1·2N-butyl-lithium (7 ml.) in ether (50 ml.) for 1 hr. Benzylideneaniline (1·4 g.) in ether (10 ml.) was then added and the solution was heated under reflux for 16 hr. The solvent was removed and the residue was extracted with chloroform. The extract was washed with water, dried, and evaporated and the residue was chromatographed on basic alumina. Elution with light petroleum gave first triphenylarsine (2 g.), m.p. and mixed m.p. 60°, and then 1,2,3-triphenylaziridine (0·8 g.), m.p. 88° (lit.,¹⁰ m.p. 88°), v_{max} . 1590, 1490, 1400, 1340, 1200, 1070, 1010, 930, 890, 760, and 695 cm.⁻¹; m/e 271, 180, and 167.

A similar experiment using benzylidene-*m*-nitroaniline (1.85 g.), gave, in order of elution, triphenylarsine (2.55 g.), 1-m-*nitrophenyl*-2,3-*diphenylaziridine* (0.6 g.), m.p. (from ethanol) 96°, v_{max} 1620, 1580, 1530, 1340, 1260, 1210, 1080, 1030, 960, 880, 850, 800, 770, 740, and 695 cm.⁻¹; *m/e* 316, 300, 270, 240, 180, and 90 (Found: C, 76·1; H, 5·2; N, 9·0. C₂₀H₁₆N₂O₂ requires C, 76·0; H, 5·1; N, 8·85%), N-benzyl-*m*-nitroaniline (0.45 g.), m.p. and mixed m.p. 107°, and *m*-nitroaniline (0.8 g.), m.p. and mixed m.p. 114°.

Alcoholysis of p-Nitrobenzyltriphenylarsonium Bromide.-A solution of the salt (2 g.) in dry ethanol (20 ml.) containing sodium (0.09 g.) was set aside at room temperature for 4 days during which the original purple colour changed to yellow. Filtration gave 4,4'-dinitrostilbene (0.04 g.), m.p. and mixed m.p. 298-302°. The filtrate was evaporated and the residue was extracted with chloroform. The extract was washed with water, dried, and evaporated and the residue was chromatographed on basic alumina. Elution with light petroleum gave triphenylarsine (0.15 g.), m.p. and mixed m.p. 60°, with light petroleum-benzene (9:1) gave p-nitrotoluene (0.35 g.), m.p. and mixed m.p. 54°, with light petroleum-ether (3:1) gave 4,4'-dintrodibenzyl (0.02 g.), m.p. and mixed m.p. 180°, and with ether-methanol gave triphenylarsine oxide (0.5 g.), m.p. and mixed m.p. 189°.

Reaction of p-Bromophenacylidenetriphenylarsorane with Dimethyl Acetylenedicarboxylate.-- A solution of p-bromophenacyltriphenylarsonium bromide (4 g.) in chloroform (50 ml.) was shaken for 4 min. with aqueous 2N-sodium hydroxide (20 ml.) and then rapidly washed free of alkali with water. The chloroform solution was dried and evaporated to give the arsorane (2.8 g.), m.p. (from ethyl acetate-light petroleum) 141-142° (Found: C, 61.9; H, 3.95. C₂₆H₂₀AsBrO requires C, 62.05; H, 3.95%). This arsorane (1.0 g.) and dimethyl acetylenedicarboxylate (0.28 g.) in tetrahydrofuran (40 ml.) were heated under reflux for 16 hr. and the solvent was evaporated off. Trituration of the residue with ether and recrystallisation from aqueous ethanol gave the *adduct* (6; $R = p-BrC_6H_4$) 995, 900, 810, and 790 cm.⁻¹; τ 6.74 (3H, s), 6.25 (3H, s), 4.15 (1H, s), and 2.0-3.0 (19H, m). Treatment of the

¹⁰ T. W. J. Taylor, J. S. Owen, and D. Whittaker, *J. Chem. Soc.*, 1938, 206.

51.25; H, 3.8. $C_{32}H_{27}AsBrClO_9$ requires C, 51.5; H, 3.6%). A similar reaction with ethoxycarbonylmethylenetriphenylarsorane at room temperature gave the *adduct* (6; $R = CO_2Et$), m.p. 146—150° (decomp., from ether), ν_{max} 1720, 1690, and 1650 cm.⁻¹, *etc*; τ 9.0 (3H, t, *J* 7 Hz), 6.7 (3H, s), 6.25 (3H, s), 6.2 (2H, q, *J* 7 Hz), 5.3 (1H, s), and 2.1—2.7 (15H, m) (Found: C, 63.0; H, 5.15; As, 14.1. $C_{28}H_{27}AsO_6$ requires C, 62.95; H, 5.05; As, 14.0%).

Reaction of p-Bromophenacylidenetriphenylarsorane with Phenylsulphine.—Benzylsulphinyl chloride (0.87 g.) in benzene (5 ml.) was added slowly to a cooled solution of the arsorane (2.5 g.) and triethylamine (0.5 g.) in benzene and the solution was set aside at room temperature for 16 hr. After filtration the filtrate was washed with water, dried, and evaporated. Crystallisation of the residue from aqueous ethanol gave benzylsulphinyl-(p-bromobenzoyl)methylenetriphenylarsorane (2.5 g.), m.p. 157—158°, v_{max} , 1580, 1565, 1495, 1440, 1015, 995, and 990 cm.⁻¹; τ 6.2 (2H, s) and 2.15—3.15 (24H, m) (Found: C, 62.0; H, 4.3; S, 5.2. C₃₃H₂₆AsBrO₂S requires C, 61.8; H, 4.0; S, 5.0%). The unusual ylide carbonyl absorption at 1495 cm.⁻¹ in Nujol moved to 1513 cm.⁻¹ in chloroform solution.

Reaction of Ethoxycarbonylmethylenetriphenylarsorane with Phenylsulphene.-Benzylsulphonyl chloride (0.48 g.) in tetrahydrofuran (5 ml.) was added slowly to a cooled solution of the arsorane (1.0 g.) and triethylamine (0.4 ml.)in tetrahydrofuran (10 ml.) and the solution was set aside at room temperature for 24 hr. G.l.c. (2-m. silicone column at 210°) then showed the presence of ethyl cinnamate (24%). When the reaction was heated under reflux for 24 hr. the yield of cinnamate was 44%. Chloroform was then added and the solution was washed with water, dried, and evaporated. Crystallisation from chloroform-ether benzylsulphonyl(ethoxycarbonyl)methylenetriphenylgave arsorane (0.3 g.), m.p. 198°, ν_{max} 1650, 1440, 1260, 1115, 1070, 1035, 1000, 975, 920, 780, and 750 cm.⁻¹; τ 9.25 (3H, t, J, 7.5 Hz), 6.1 (2H, q, J 7.5 Hz), 5.45 (2H, s), and 2·1-3·0 (20H, m) (Found: C, 62·7; H, 5·0; S, 5·4. C₂₉H₂₇-AsO4S requires C, 63.7; H, 4.95; S, 5.7%). Chromatography of the mother liquors on neutral alumina gave triphenylarsine (0.2 g.), ethyl cinnamate (0.06 g.), and the above adduct (0.13 g.).

We thank the S.R.C. for a research studentship.

[0/1634 Received, September 22nd, 1970]