[CONTRIBUTION FROM MELLON INSTITUTE]

The Chemistry of Ylids. IV. Triphenylarsoniumfluorenylide[1]

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Received September 9, 1959

Triphenylarsoniumfluorenylide (IIIe), the first example of an isolable arsenic-containing ylid, has been prepared. Its chemical and physical properties have been examined.

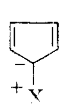
Although the reaction of ylids of type I (X = $(C_6H_5)_3P$) with carbonyl compounds

$$\underset{\text{Ia}}{\overset{+}{X} - \overset{-}{R}} \longleftrightarrow \underset{\text{Ib}}{X = R}$$

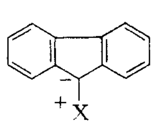
X = heteroatom group
R = hydrocarbon group

was discovered in 1919 by Staudinger and Meyer,[2] it is only recently that its full scope and potential have been realized. Wittig and co-workers[3] demonstrated the synthetic usefulness of triphenylphosphoniummethylide (I, X = $(C_6H_5)_3P$, R = CH_2) and its derivatives as olefin-forming reagents. Since that time numerous examples of the preparation and reactions of these ylids have been reported.[4]

Few isolable, crystalline ylids have been characterized. In the phosphorus series triphenylphosphoniumbenzylide (I, X = $(C_6H_5)_3P$, R = C_6H_5CH),[5] triphenylphosphoniumbenzhydrylide (I, X = $(C_6H_5)_3P$, R = $C(C_6H_5)_2$),[6] triphenylphosphoniumcyclopentadienylide (IIa),[7] triphenylphosphoniumfluorenylide (IIIa),[1a] and tributylphosphoniumfluorenylide (IIIb)[8] are known. In the sulfur series, only dimethylsulfoniumfluorenylide (IIIc)[1c,9a] and its 2,7-dinitro derivative[9b] have been described. Three nitrogen ylids, trimethylammoniumcyclopentadienylide (IIb),[10] 1-pyridiniumcyclopentadienylide (IIc)[11] and 1-pyridiniumfluorenylide (IIId)[12] have been prepared and isolated. However, none of this latter group is comparable in stability to the phosphorus and sulfur ylids.



IIa. X = $(C_6H_5)_3P$
IIb. X = $(CH_3)_3N$
IIc. X = 1-pyridinium



IIIa. X = $(C_6H_5)_3P$
IIIb. X = $(C_4H_9)_3P$
IIIc. X = $(CH_3)_2S$
IIId. X = 1-pyridinium
IIIe. X = $(C_6H_5)_3As$
IIIf. X = $(CH_3)_3As$

The unique stability of phosphorus- and sulfur-containing ylids is attributed to *d*-orbital resonance. This phenomenon depends on the ability of these hetero atoms to expand their octet to a decet by accepting an electron pair from a carbon 2*p*-orbital into a vacant sulfur or phosphorus 3*d*-orbital, thereby allowing the contribution of structure Ib as well as Ia to the resonance hybrid. If such is in fact the case, one may select other hetero atoms which should behave similarly and expect to produce stable, isolable ylids from a properly constructed molecule. Accordingly, we have undertaken to examine the ability of arsenic-containing compounds to form stable ylids and to compare their behavior to the phosphorus analog.

There is but little evidence in the literature concerning the ability of arsenic to expand its octet. By examining the deuteroxide-catalyzed exchange of deuterium in tetramethylphosphonium and trimethylsulfonium salts, Doering and Hoffmann[13] concluded that the heats of activation were lowered from the expected values (calculated on the basis of coulombic interactions only) by 15.4 and 17.2 kcal., respectively. This lowering was ascribed to *d*-orbital resonance in each case. In a less precise but analogous manner they indicated that in proceeding down the group V elements, the contribution of *d*-orbital resonance should remain nearly constant, the rate of exchange decreasing in proportion to and due solely to the increased bond distance. Chatt and co-workers[14] claimed that ar-

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(1) For previous papers in this series see (a) III, A. W. Johnson, *J. Org. Chem.*, **24**, 282 (1959); (b) II, A. W. Johnson and R. B. LaCount, *Chem. and Ind.*, 52 (1959); (c) I, A. W. Johnson and R. B. LaCount, *Chem. and Ind.*, 1440 (1958).

(2) H. Staudinger and J. Meyer, *Helv.*, **2**, 619 (1919).

(3) G. Wittig and U. Schollkopf, *Ber.*, **87**, 1318 (1954) and succeeding papers.

(4) For a recent review of this reaction see J. Levisalles, *Bull. Soc. Chim.*, 1020 (1958).

(5) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

(6) C. S. Marvel and C. Coffmann, *J. Am. Chem. Soc.*, **51**, 3496 (1929).

(7) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957).

(8) A. W. Johnson and R. B. LaCount, *Tetrahedron*, in press.

(9) (a) C. K. Ingold and J. H. Jessop, *J. Chem. Soc.*, 713 (1930); (b) E. D. Hughes and K. I. Kuriyan, *J. Chem. Soc.*, 1609 (1935).

(10) H. J. Dauben, Jr., Abstracts, American Chemical Society 126th meeting, pp. 18–O, September 1954.

(11) D. Lloyd and J. S. Sneezum, *Tetrahedron*, **3**, 334 (1958).

(12) F. Krohnke, *Ber.*, **83**, 253 (1950).

(13) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(14) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).

sines participate in double bonding (*via* 4*d*-orbitals) to nearly the same extent as phosphines when used as ligands for complexes of certain metal ions. They presumed that the π-bond was formed by the donation of electrons from a filled *d*-orbital of the metal to the vacant 4*d*-orbital of arsenic.

As mentioned previously, most phosphorus ylids examined to date have been nonisolable, relatively unstable compounds necessitating their preparation *in situ*. It is difficult, however, to obtain reliable quantitative data from the reaction of these ylids with other compounds. It is obviously desirable to utilize stable, readily isolable ylids in these studies. Furthermore, it permits examination of their physical properties.

In this regard, Ramirez and Levy[7] prepared and examined the chemistry of triphenylphosphoniumcyclopentadienylide (IIa), an extremely stable, high melting solid. However, they were unable to effect a Wittig reaction between IIa and benzaldehyde, the electronic configuration of the former preferring to maintain its *status quo* as a pseudoaromatic system. In an effort to circumvent this difficulty we recently examined the chemistry of triphenylphosphoniumfluorenylide (IIIa).[1a] This crystalline ylid did undergo the Wittig reaction with selected carbonyl compounds, the sequence of which shed some light on the mechanism of this reaction.

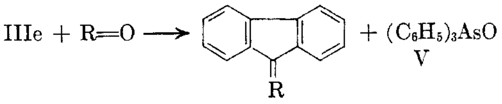
We chose to employ the fluorene nucleus as the hydrocarbon portion (I, R = fluorenylidene) in all our studies for several reasons. The expected products from a Wittig reaction were, for the most part, well characterized, crystalline compounds. In addition, the convenient electronic properties of this nucleus conferred on an ylid enough stability to permit isolation and modified the reactivity so as to permit some selectivity in the rate and facility of reaction. Further instances of these effects are evidenced by the behavior of IIIb[8] and IIIc.[1c] As a result of these successes we are continuing this approach and now wish to report on the chemistry of triphenylarsoniumfluorenylide (IIIe).

Only two arsenic-containing ylids have been reported to date, neither of which underwent a normal Wittig reaction. In 1953 Wittig and Laib[15] prepared solutions of trimethylarsoniumfluorenylide (IIIf) but found that 9-fluorenyldiphenylcarbinol, the result of simple carbanion addition, was the sole product from reaction with benzophenone. In addition, they found the ylid hydrolyzed to fluorene and trimethylarsine oxide on contact with water.

In a preliminary report Wittig and Henry[16] indicated that reaction between triphenylarsoniummethylide (I, X = $C_6H_5)_3As$, R = CH_2) and benzophenone afforded a mixture of diphenylethylene, the normal product, and, in predominant amounts, diphenylacetaldehyde. It is possible to rationalize the unexpected aldehyde formation *via* an intermediate 1,1-diphenylethylene oxide presumably formed in an analogous manner to those from sulfur ylid reactions.[1c]

Treatment of triphenylarsine with 9-bromofluorene[17] afforded an 83% yield of triphenylfluorenylarsonium bromide. Upon dissolution of the salt in ethanol, followed by the addition of an equivalent amount of aqueous sodium hydroxide solution, triphenylarsoniumfluorenylide (IIIe) precipitated as bright yellow plates in 88% yield. We were unable to obtain satisfactory analytical data for this ylid. However, its mode of formation together with its physical and chemical properties left little doubt as to its constitution. The ylid, m.p. 188–190°, dissolved in dilute mineral acid forming a colorless solution from which it could be reprecipitated unchanged upon the addition of alkali. Its ultraviolet spectrum in chloroform solution was very similar to that of the phosphorus analog (IIIa).[1a] The ylid was hydrolyzed only by heating under reflux with ethanolic sodium hydroxide solution over long periods of time. Chromatography of the reaction mixture afforded fluorene and triphenylarsine oxide in 69% and 43% yields, respectively. A sample of the latter compound was prepared unambiguously by permanganate oxidation of triphenylarsine.

In order to test the reactivity of the ylid (IIIe) in the Wittig reaction and to permit a comparison with the phosphorus analog (IIIa),[1a] the former was treated with a series of carbonyl compounds to produce the fluorenylidene derivatives (IV) and triphenylarsine oxide (V). These results are summarized in Table I.



IVa. R = CHC_6H_5
IVb. R = p-$NO_2C_6H_4CH$
IVc. R = p-ClC_6H_4CH
IVd. R = p-$CH_3OC_6H_4CH$
IVe. R = p-$(CH_3)_2NC_6H_4CH$
IVf. R = $C(C_6H_5)_2$
IVg. R = $C(CH_3)_2$
IVh. R = $CHCH_3$

It is apparent that the ylid (IIIe) distinguishes between aldehydes and ketones as effectively as did the phosphorus analog (IIIa).[1a] However, in contrast to the latter with which the reactivity sequence with *para*-substituted benzaldehydes clearly was p-$NO_2 > Cl > H > OCH_3 > N(CH_3)_2$, the arsenic ylid (IIIe) reacted with all benzaldehydes in nearly equal yields. For example, the phosphorus analog (IIIa) failed to react with p-dimethylaminobenzaldehyde whereas IIIe reacted in 97%

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[15] G. Wittig and H. Laib, *Ann.*, **580**, 57 (1953).

[16] G. Wittig and M. C. Henry, Abstracts, American Chemical Society 135th meeting, pp. 67–O, April 1959.

[17] G. Wittig and G. Felletschin, *Ann.*, **555**, 133 (1944).

TABLE I

CONDENSATION OF IIIe WITH CARBONYLS

Reactant	Yield of Product, %	Expected Product	Yield of Oxide (V), %
Benzaldehyde	74	IVa	37
p-Nitrobenzaldehyde	92	IVb	26
p-Chlorobenzaldehyde	98	IVc	98
p-Anisaldehyde	89	IVd	65
p-Dimethylaminobenzaldehyde	97	IVe	51
Benzophenone	0	IVf	0
Acetone	0	IVg	0
Acetaldehyde	91	IVh	78

yield to produce *p*-dimethylaminobenzalfluorene (IVe). Furthermore, we isolated only the expected "Wittig reaction" products, finding no evidence of any ketonic products as would be expected if Wittig and Henry's observations[16] with arsenic-containing ylids were applied to this ylid (IIIe).

We conclude that arsenic and phosphorus differ slightly in their contribution to the stabilization and reactivity of ylids and therefore differ in their extent of *d*-orbital resonance. From mechanistic considerations it is clear that tetracovalent phosphorus undergoes octet expansion (*d*-orbital resonance) to a greater degree than does similarly substituted arsenic.

EXPERIMENTAL[18]

Triphenylfluorenylarsonium bromide. A solution of 6.25 g. (0.02 mol.) of triphenylarsine and 5.0 g. (0.02 mol.) of 9-bromofluorene[17] in 100 ml. of nitromethane was warmed on a steam bath for 1 hr. The nitromethane was removed *in vacuo* and 100 ml. of acetone was added, resulting in the formation of a colorless precipitate (9.3 g., 83% yield). Recrystallization from benzene-ethanol afforded *triphenylfluorenylarsonium bromide* as colorless microcrystals, m.p. 178–179.5°.

Anal. Calcd. for $C_{31}H_{24}AsBr$: C, 67.5; H, 4.4; As, 13.6; Br, 14.5. Found: C, 66.5; H, 4.6; As, 13.9; Br, 14.9.

The salt gave a positive test for ionic halogen and afforded a yellow precipitate (ylid) when treated with ammonia solutions. The salt was not affected by refluxing in aqueous solution.

Triphenylarsoniumfluorenylide (IIIe). To a stirred solution of 7.2 g. (0.013 mol.) of the above bromide in 500 ml. of absolute ethanol was added portionwise at room temperature 5 ml. of 2.5*N* sodium hydroxide solution. A copious yellow precipitate appeared which was removed by filtration and dried to constant weight (4.7 g., 78% yield). Recrystallization from benzene-hexane afforded *triphenylarsoniumfluorenylide* (IIIe) as fine yellow plates, m.p. 188–190° dec.

Anal. Calcd. for $C_{31}H_{23}As$: C, 79.1: H, 5.0; As, 15.9. Found: C, 80.4; H, 5.3; As, 13.6.

Ultraviolet spectrum: $\lambda_{\max}^{CHCl_3}$ 250 mμ (log ϵ 4.74), 258 mμ (log ϵ 4.86), 294 mμ (log ϵ 3.74) and 390 mμ (log ϵ 3.15).

Hydrolysis of the ylid (IIIe). A heterogeneous solution of 0.55 g. (1.17 mmol.) of ylid in 25 ml. of ethanol containing 5 ml. of 2.5*N* sodium hydroxide solution was heated under reflux for 18 hr. The now homogeneous solution was quenched with water and extracted with ether. The etheral solution was dried and the solvent removed leaving 0.43 g. of pale yellow solid. This was chromatographed on 15 g. of alumina. Elution with benzene afforded 0.13 g. of colorless solid which crystallized from 95% ethanol as colorless plates, m.p. 115–116°, undepressed on admixture with an authentic sample of fluorene. Elution with methanol afforded 0.15 g. pale yellow solid which crystallized from water as colorless needles, m.p. 189–191°, undepressed on admixture with an authentic sample of triphenylarsine oxide.

Triphenylarsine oxide (V). A solution of 1.0 g. (3.3 mmol.) of triphenylarsine and 1.0 g. (6.6 mmol.) of potassium permanganate in 60 ml. of 50% acetone-water solution was warmed on a steam bath for 5 hr. The solution was cooled, filtered through celite and the filtrate evaporated. Filtration of the resulting aqueous slurry afforded 0.6 g. (57%) of *triphenylarsine oxide* which was recrystallized from water as colorless needles, m.p. 193.5–195.5°, (lit.[19] m.p. 192°).

Anal. Calcd. for $C_{18}H_{15}AsO$: C, 67.1; H, 4.7; As, 23.3. Found: C, 66.5; H, 5.1; As, 22.8.

Reaction of IIIe with carbonyl compounds. A standard procedure was used in all reactions. To a solution of 0.47 g. (1.0 mmol.) of ylid (IIIe) in 20 cc. of chloroform was added 1.0 mmol. of carbonyl compound. After heating under reflux for 3 hr. the solvent was evaporated on a steam bath. The residue was taken up in benzene and chromatographed on 10 g. of alumina. The individual fractions were purified further by recrystallization.

A. Benzaldehyde (0.11 g.) and IIIe were treated as described. Elution with 50% benzene-hexane solution afforded 0.19 g. (74%) of benzalfluorene (IVa) which was recrystallized from 80% ethanol-water as pale yellow needles, m.p. 73–74°, undepressed on admixture with an authentic sample (lit.[20] m.p. 76°). Elution with methanol afforded 0.10 g. (37%) of triphenylarsine oxide (V) which crystallized from water as colorless microcrystals, m.p. 192–194°, undepressed on admixture with an authentic sample.

B. *p*-Nitrobenzaldehyde (0.15 g.) was treated with IIIe as described. Elution with benzene afforded 0.28 g. (92%) of *p*-nitrobenzalfluorene (IVb) which crystallized from ethanol as fine yellow needles, m.p. 167–168°, undepressed admixture with an authentic sample (lit.[21] m.p. 167°). Elution with methanol afforded 0.07 g. (26%) of triphenylarsine oxide (V). It crystallized from water as colorless needles, m.p. 191–193°, undepressed on admixture with an authentic sample.

C. *p*-Chlorobenzaldehyde (0.14 g.) and IIIe were treated as described. Elution with benzene afforded 0.28 g. (98%) of *p*-chlorobenzalfluorene (IVc) which crystallized from ethanol as pale yellow microcrystals, m.p. 147–148° (lit.[22] m.p. 149°).

Anal. Calcd. for $C_{20}H_{13}Cl$: C, 83.2; H, 4.5; Cl, 12.3. Found: C, 82.9; H, 4.7; Cl, 11.8.

Elution with methanol afforded 0.32 g. (98%) of triphenylarsine oxide (V) which crystallized from water as colorless needles, m.p. 190–192°, undepressed on admixture with an authentic sample.

D. *p*-Anisaldehyde (0.14 g.) and IIIe were treated as described. Elution with benzene afforded 0.16 g. (89%) of *p*-anisalfluorene (IVd) which crystallized from ethanol as pale yellow plates, m.p. 130.5–132.5°, undepressed on admixture with an authentic sample (lit.[23] m.p. 128–129°). Elution with methanol afforded 0.13 g. (65%) of triphenyl-

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[18] Melting points are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Ultraviolet spectra were recorded by a Cary model 14 spectrophotometer. All chromatograms were run on Merck alumina, No. 71707.

[19] M. P. Pascal, *Bull. Soc. Chim.*, [4], **33**, 171 (1923).

[20] J. Thiele, *Ber.*, **33**, 851 (1900).

[21] E. D. Bergmann *et al.*, *Bull. Soc. Chim.*, **19**, 705 (1952).

[22] A. Sieglitz, *Ber.*, **52**, 1513 (1919).

[23] J. Thiele and F. Henle, *Ann.*, **347**, 290 (1906).

arsine oxide (V) which crystallized from water as colorless needles m.p. 186–188°, undepressed on admixture with an authentic sample.

E. *p*-Dimethylaminobenzaldehyde (0.15 g.) and IIIc were treated as described. Elution with 50% benzene-chloroform afforded 0.29 g. (97%) of *p*-dimethylaminobenzalfluorene (IVe) which crystallized from ethanol as yellow microcrystals, m.p. 135–135.5° (lit.[21] m.p. 135–136°).

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.8; H, 6.5; N, 4.7. Found: C, 88.6; H, 6.7; N, 4.6.

Elution with methanol afforded 0.16 g. (51%) of triphenylarsine oxide (V) which crystallized from water as colorless needles, m.p. 190–192°, undepressed on admixture with an authentic sample.

F. Acetaldehyde (0.30 g.) and IIIe were dissolved in 20 ml. of chloroform and the solution was heated in a sealed tube for 3 hr. The usual workup followed. Elution with benzene afforded 0.26 g. (91%) of 9-ethylidenefluorene (IVh) which crystallized from ethanol-water as colorless needles, m.p. 102–104°, undepressed an admixture with an authentic sample (lit.[24] m.p. 104°). Elution with methanol afforded 0.37 g. (78%) of triphenylarsine oxide (V) which crystallized from water as colorless needles, m.p. 191–194°, undepressed an admixture with an authentic sample.

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[24] F. Mayer, *Ber.*, **46**, 2579 (1913).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INDIAN INSTITUTE OF SCIENCE]

Synthesis of Cyclohexylideneacetaldehyde and 2-, 3- and 4-Methylcyclohexylideneacetaldehyde

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Received July 27, 1959

Cyclohexanone and 2-, 3- and 4-methylcyclohexanones have been condensed with acetylene to give the respective 1-ethinylcyclohexanols. The 1-ethinylcyclohexanols were hydrogenated to the respective 1-vinyl- and 1-ethylcyclohexanols. The 1-vinylcyclohexanols have been treated with phosphorus tribromide to give the corresponding rearranged β-cyclohexylidenethyl bromides which have been converted to the pyridinium salts. The latter were treated with *p*-nitrosodimethylaniline and alkali (Krohnke's method) to give the corresponding nitrones which were hydrolyzed to the corresponding aldehydes. The 1-ethinyl-, 1-vinyl- and 1-ethylcyclohexanols prepared were subjected to pharmacological tests.

In attempts to extend the application of Krohnke's method of synthesis of aldehydes[1] to the preparation of α,β-unsaturated aldehydes in the aliphatic and alicyclic series, the reaction conditions were first studied using cinnamyl bromide and geranyl bromide.[2] The optimum conditions thus obtained have been used for the preparation of cyclohexylideneacetaldehyde and 2-, 3- and 4-methylcyclohexylideneacetaldehydes.[3]

Cyclohexylideneacetaldehyde has been prepared by other workers by chromic acid oxidation of β-cyclohexylideneethanol (Dimroth[4]) and from 1-allylcyclohexanol by ozonization (Aldersley *et al.*,[5] Braude and Wheeler[6]). Braude and Wheeler[6] describe its preparation from cyclohexanone by the ethoxyacetylene method. These workers prepared 2-methylcyclohexylideneacetaldehyde by similar methods.[6 *cf.* 7–9]

The cyclohexanones (cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone) were first condensed with acetylene in the presence of sodium acetylide in liquid ammonia to give the corresponding 1-ethinylcyclohexanols. The three methyl 1-ethinylcyclohexanols can exist in *cis* and *trans* forms. Two forms (solid and liquid) of both 2- and 4-methyl-1-ethinylcyclohexanols have been reported.[10–13] In the present study these carbinols also have been separated into solid and liquid forms. Rupe and co-worker[14] prepared solid (m.p. 47.5°) and liquid forms of optically active 3-methyl-1-ethinylcyclohexanol. Following their procedure the

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[1] F. Krohnke and E. Borner, *Ber.*, **69**, 2006 (1936); F. Krohnke, *Angew. Chem.*, **65**, 612 (1953).

[2] M. C. Chaco and B. H. Iyer, *J. Indian Inst. Sci.*, **36**, No. 3, 160 (1954). (Part of the work is in press).

[3] The work is outlined in preliminary communications, *Chem. & Ind.* (*London*), 155 (1956); *Curr. Sci.* (*India*), **22**, 240 (1953).

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[6] E. A. Braude and D. H. Wheeler, *J. Chem. Soc.*, 320 (1955).

[7] H. Rupe and E. Kambli, *Helv. Chim. Acta*, **9**, 672 (1926); H. Rupe, W. Messner, and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

[8] F. G. Fisher and K. Lowenberg, *Ann.*, **475**, 203 (1929); C. D. Hurd and R. E. Christ, *J. Am. Chem. Soc.*, **59**, 118 (1937).

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[13] J. D. Billimoria and N. F. Maclagan, *J. Chem. Soc.*, 3257 (1954).

[14] H. Rupe and E. Kambli, *Ann.*, **459**, 195 (1927).