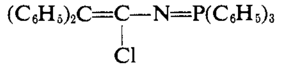
Synthesis and Reactions of Allenic Phosphonium Salts and Ylides

K. W. Ratts and R. D. Partos

Contribution from the Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166. *Received May 2, 1969*

Abstract: 2-Bromo-3,3-diphenylallyltriphenylphosphonium bromide, upon treatment with 1 equiv of base, yields 3,3-diphenylallenyltriphenylphosphonium bromide, whereas excess base produces, *in situ*, a cumulative ylide (**15**). The allenylphosphonium salt is unreactive to methyl alcohol and *t*-butyl mercaptan, but adds aniline. This latter adduct can be dehydrohalogenated to an imino-stabilized phosphorus ylide (**12**) which reacts with aromatic aldehydes *via* the Wittig reaction. The cumulative ylide (**15**) undergoes Wittig reactions with aromatic aldehydes, aromatic isocyanates, and diphenylketene.

The reaction of chlorodiphenylacetonitrile with triphenylphosphine has been described.[1] The reactive intermediate (**1**) which is formed has been shown to react with nucleophiles such as alcohols, mercaptans, amines, and carboxylic acids. Because it seemed probable that **1** existed as an α-halovinylphosphinimine



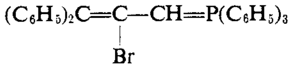
$$(C_6H_5)_2C{=}\underset{Cl}{\underset{|}{C}}{-}N{=}P(C_6H_5)_3$$

1

rather than a ketiminephosphonium salt (**2**) it was of interest to prepare and study the chemistry of an α-halovinyl ylide (**3**).

$$(C_6H_5)_2C{=}C{=}N{-}\overset{+}{P}(C_6H_5)_3\ Cl^-$$

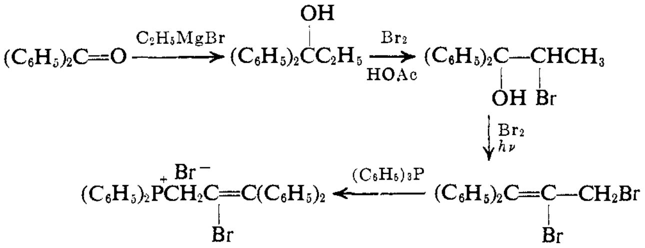
2



$$(C_6H_5)_2C{=}\underset{Br}{\underset{|}{C}}{-}CH{=}P(C_6H_5)_3$$

3

1,1-Diphenyl-2,3-dibromopropene-1 (**4**) was prepared by the route shown below[2] and converted to the phosphonium salt (**5**) by treatment with triphenylphosphine.



$$(C_6H_5)_2C{=}O \xrightarrow{C_2H_5MgBr} (C_6H_5)_2\overset{OH}{\overset{|}{C}}C_2H_5 \xrightarrow[HOAc]{Br_2} (C_6H_5)_2\underset{OH}{\underset{|}{C}}{-}\underset{Br}{\underset{|}{C}}HCH_3 \xrightarrow[h\nu]{Br_2} (C_6H_5)_2C{=}\underset{Br}{\underset{|}{C}}{-}CH_2Br \xrightarrow{(C_6H_5)_3P} (C_6H_5)_3\overset{+}{P}CH_2\underset{Br}{\underset{|}{C}}{=}C(C_6H_5)_2\ Br^-$$

5 **4**

A doublet ($J_{^{31}PH}$ = 14 cps, area = 2) at τ 5.1 for the methylene protons of the product **5** indicates no isomerization[3] to the propenyl salt has occurred. The salt **5** could not be recrystallized without apparent complex formation; however, it was possible to purify the corresponding perchlorate.

Dehydrohalogenation of **5** by heating with diglyme or treatment with triethylamine gave the allenylphosphonium salt **6**. The salt **6** exhibits an allene peak at 5.21 μ in the ir spectrum and a doublet at τ 1.3 (*J* = 9 cps) for the allenic proton resonance in the nmr spectrum.

$$5 \xrightarrow{\text{base}} (C_6H_5)_2C{=}C{=}CH{-}\overset{+}{P}(C_6H_5)_3\ \ Br^-$$

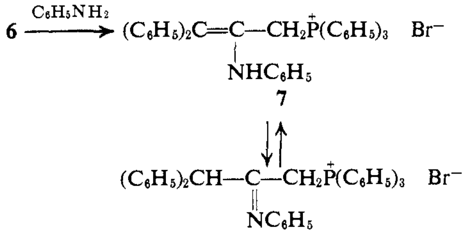
6

All attempts to convert **5** to the α-bromovinyl ylide **3** have failed. The preference for structure **6** over **3** is in contrast to the situation with the imine counterparts where **1** is preferred over **2**.

Seyferth[4] prepared vinyltriphenylphosphonium bromide by the treatment of 2-bromoethyltriphenylphosphonium bromide with moist silver oxide. This represents an analogy for dehydrohalogenation of a phosphonium salt to an unsaturated phosphonium salt instead of to an ylide.

$$BrCH_2CH_2\overset{+}{P}(C_6H_5)_3\ \ Br^- \xrightarrow{Ag_2O} CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\ \ Br^-$$

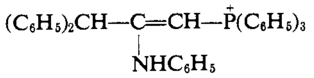
The allenic phosphonium salt **6** was essentially unchanged after 0.5 hr in refluxing methanol and on treatment with *t*-butyl mercaptan. In contrast aniline resulted in an adduct characterized as **7** or **8** rather than the enaminophosphonium salt **9**. The alternate possible structure **9** was eliminated on the basis of the nmr spectrum of the derived perchlorate salt which exhibits a methylene doublet at τ 5.4 (*J* = 14 cps) inconsistent with a vinylphosphonium salt.



$$6 \xrightarrow{C_6H_5NH_2} (C_6H_5)_2C{=}\underset{NHC_6H_5}{\underset{|}{C}}{-}CH_2\overset{+}{P}(C_6H_5)_3\ \ Br^- \ \rightleftharpoons\ (C_6H_5)_2CH{-}\underset{NC_6H_5}{\underset{\|}{C}}{-}CH_2\overset{+}{P}(C_6H_5)_3\ \ Br^-$$

7

8



$$(C_6H_5)_2CH{-}\underset{NHC_6H_5}{\underset{|}{C}}{=}CH{-}\overset{+}{P}(C_6H_5)_3$$

9

Treatment of **7** with aqueous base results in fragmentation. The ir spectrum of the products indicates the presence of diphenylallene, aniline, and triphenylphosphine oxide.

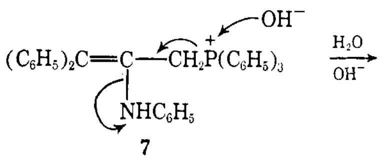
---

[1] R. D. Partos and K. W. Ratts, *J. Amer. Chem. Soc.*, **88**, 4996 (1966).

[2] V. I. Pansevich-Kolyada, *J. Gen. Chem. USSR*, 30, 3854 (1960).

[3] Allyltriphenylphosphonium halides undergo thermal isomerization to propenylphosphonium salts. After 17 hr in refluxing xylene, allyltriphenylphosphonium bromide was *ca.* 48% isomerized to the propenyl derivative. There was no trace of allyltriphenylphosphonium chloride in propenyltriphenylphosphonium chloride prepared by refluxing allyl chloride and triphenylphosphine 18 hr in xylene.

[4] D. Seyferth, J. S. Fogel, and J. K. Heeren, *J. Amer. Chem. Soc.*, **86**, 307 (1964).

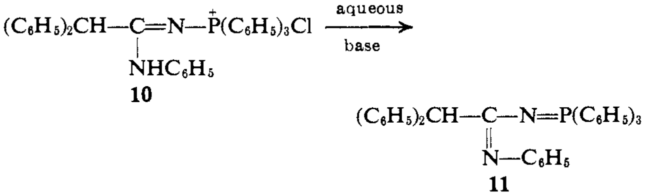


7

$$(C_6H_5)_2C{=}\underset{\substack{|\\ NHC_6H_5}}{C}{-}CH_2\overset{+}{P}(C_6H_5)_3 \quad \overset{OH^-}{} \quad \xrightarrow[OH^-]{H_2O}$$

$$(C_6H_5)_2C{=}C{=}CH_2 \;+\; C_6H_5NH_2 \;+\; (C_6H_5)_3P{=}O$$

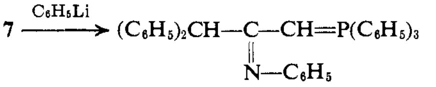
This behavior was not observed in the analogous salt **10** where aqueous base treatment led to the iminophosphinimine **11**.[1] However, treatment of **7** with phenyllithium gave rise to the expected dehydrohalogenation product, the imino ylide **12**. The nmr spectrum of **12** exhibits an aromatic multiplet at τ 2.1–3.2, a quartet at τ 3.85, and a doublet (J = 4 cps) at τ 4.8. The doublet at τ 4.8 was assigned to the benzhydryl proton, which appears at τ 4.85 in phosphinimine **11**. The quartet at τ 3.85 must be assigned to the two *ortho* protons on the nitrogen-bonded benzene ring (which appear at τ 3.6 in **11**) and the methine proton α to the phosphorus atom. The downfield shift of this hydrogen and the upfield shift of the *ortho* hydrogens is due to the significant contribution **12a** must make to the resonance hybrid. The ir spectrum of **12** exhibited no NH peak but had strong absorption at 6.57, 7.25, and 9.07 μ. For purposes of comparison **13** exhibited strong peaks at 6.53, 7.19, and 9.08 μ.[5]



10

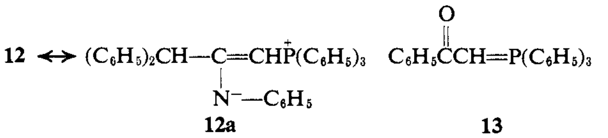
11

$$(C_6H_5)_2CH{-}\underset{\substack{|\\ NHC_6H_5}}{C}{=}N{-}\overset{+}{P}(C_6H_5)_3Cl \xrightarrow[\text{base}]{\text{aqueous}} (C_6H_5)_2CH{-}\underset{\substack{\|\\ N-C_6H_5}}{C}{-}N{=}P(C_6H_5)_3$$



12

$$7 \xrightarrow{C_6H_5Li} (C_6H_5)_2CH{-}\underset{\substack{\|\\ N-C_6H_5}}{C}{-}CH{=}P(C_6H_5)_3$$

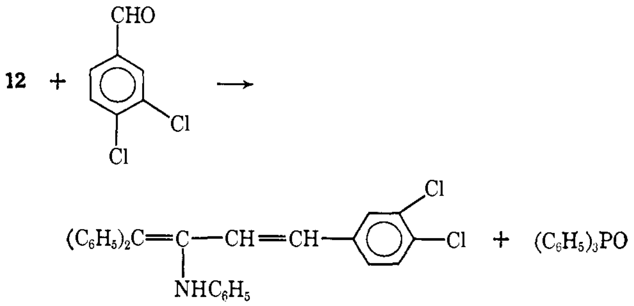


12a

13

$$12 \longleftrightarrow (C_6H_5)_2CH{-}\underset{\substack{|\\ N^--C_6H_5}}{C}{=}CH\overset{+}{P}(C_6H_5)_3 \qquad C_6H_5\overset{\substack{O\\ \|}}{C}CH{=}P(C_6H_5)_3$$

When **12**, an imino-stabilized phosphorus ylide, was treated with 3,4-dichlorobenzaldehyde, there was obtained a 75% yield of triphenylphosphine oxide and a 52% yield of a yellow solid identified as the enamine **14**.



14

The ir spectrum shows NH absorption at 2.96 μ and a strong band at 6.26 μ.[6] The nmr spectrum exhibits the NH as a broad singlet at τ 4.7, whereas the vinyl hydrogens are obscured by the aromatic absorption at τ 2.5–3.4.

Treatment of **5** or **6** with excess pyridine results in formation of a cumulative ylide (**15**). Attempts to isolate **15** yield only unchanged starting salt **6**, suggesting that the cumulative ylide is actually present only in very small amounts in pyridine. Solutions of **15** may also be prepared by treatment of **5** or **6** with triethylamine in acetonitrile. Triethylamine hydrobromide crystallizes out of solution, but attempts to isolate **15** were unsuccessful.

$$5 \xrightarrow{\text{pyridine}} 6 \xrightarrow{\text{pyridine}} [(C_6H_5)_2C{=}C{=}C{=}P(C_6H_5)_3]$$

15

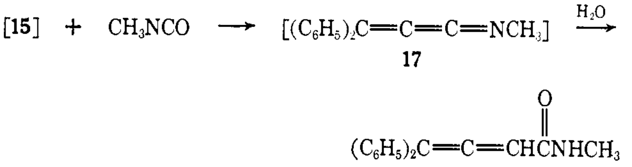
The cumulative ylide **15** has been found to undergo a number of Wittig-type reactions. Addition of aromatic aldehydes to a solution of **15** in acetonitrile affords excellent yields of the corresponding cumulenes (**16**).

$$[15] + ArCHO \longrightarrow (C_6H_5)_2C{=}C{=}C{=}CHAr$$

16a, Ar = $4\text{-}NO_2C_6H_4$
b, Ar = $3,4\text{-}Cl_2C_6H_3$

The cumulenes exhibit a band in the ir spectrum at 4.91 μ and the cumulene proton absorbs at *ca.* τ 3.7 in the nmr spectrum.

Reaction of **15** (in triethylamine–acetonitrile) with methyl isocyanate, followed by treatment with water, yielded the allenyl amide **18** in *ca.* 28% yield, presumably *via* the cumulative ketenimine **17**. The ir spectrum of **18** exhibited an allene band at 5.21 μ and a carbonyl band at 6.0 μ. In the nmr spectrum the allenic proton appeared as a singlet at τ 3.98, the amide proton as a broad peak at 4.2, and the N-methyl as a doublet (J = 4.5 cps) at 7.2. This splitting of the N-methyl resonance must be due to spin coupling of the N-methyl and N–H protons since no coalescence occurs at elevated temperatures.



17

18

$$[15] + CH_3NCO \longrightarrow [(C_6H_5)_2C{=}C{=}C{=}NCH_3] \xrightarrow{H_2O} (C_6H_5)_2C{=}C{=}CH\overset{\substack{O\\ \|}}{C}NHCH_3$$

The reaction of ylide **15** with diphenylketene produced the dimer of the expected tetraphenylpentatetraene (**19**).

$$[15] + (C_6H_5)_2C{=}C{=}O \longrightarrow (C_6H_5)_2C{=}C{=}C{=}C{=}C(C_6H_5)_2 \longrightarrow \text{dimer}$$

19

The cumulene **19** has been previously prepared by Kuhn,[7] as has the dimer by Fischer.[8] The elementary analysis, molecular weight, and melting point are correct for the dimer. The uv spectrum exhibited maxima at 296 (log ε 4.56) and 370 mμ (log ε 3.77) *vs.* a reported[8] λ_{max} 297 (log ε 4.88) and 385 mμ (log ε 3.77). The pentatetraene is much more susceptible to dimerization than the butatriene or hexapentaene are.[8]

Gilman[9] has prepared an allenic ylide **20** by treatment of 2,2-diphenylvinyltriphenylphosphonium bro-

---

(5) A. J. Speziale and K. W. Ratts, *J. Org. Chem.*, **28**, 465 (1963).

(6) The crude material also exhibits a ketenimine band in the ir spectrum at 4.71 μ.

(7) R. Kuhn, H. Fischer, and H. Fischer, *Chem. Ber.*, **97**, 1760 (1964).

(8) H. Fischer and H. Fischer, *ibid.*, **97**, 2959 (1964).

(9) H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

mide with phenyllithium. Reaction of **20** with benzophenone yielded tetraphenylallene.

$$(C_6H_5)_2C{=}CH\overset{+}{P}(C_6H_5)_3Br \xrightarrow{C_6H_5Li}$$

$$\underset{\textbf{20}}{(C_6H_5)_2C{=}C{=}P(C_6H_5)_3} \longrightarrow (C_6H_5)_2C{=}C{=}C(C_6H_5)_2$$

No reaction occurred when **15** was treated with benzophenone. The decreased reactivity of **15** relative to **20** is probably due to the greater conjugation in **15**.

The synthesis and reations of allenic phosphonium salts and ylides illustrate another potentially useful aspect of Wittig reagent chemistry.

Experimental Section[10]

1,1-Diphenylpropanol-1. To a slurry of 25 g of magnesium in 150 ml of anhydrous ether was slowly added 109 g of ethyl bromide in 375 ml of ether. The mixture was refluxed for 45 min after addition was complete, and then 182 g of benzophenone in 375 ml of ether was slowly added, the temperature being kept at 10–15° during addition. The reaction mixture was poured onto ice, neutralized with ammonium chloride, and extracted with ether. The ether extracts were washed, dried, and evaporated to an oily solid. Recrystallization from hexane afforded 122 g (58%) of the alcohol, mp 86–92° (lit.[11] mp 94–95°).

1,1-Diphenyl-2-bromopropanol-1. The procedure of Pansevich-Kolyada[12] was followed, with minor modifications. Bromine, 7.7 g (0.048 mol), in 10 ml of 80% acetic acid was slowly added to a warm solution of 10 g (0.047 mol) of 1,1-diphenylpropanol-1 in 50 ml of 80% acetic acid. The temperature was maintained at 60–70°. After addition was complete the reaction was stirred at 70° for 5 min and then poured into 300 ml of cold water. The mixture was neutralized with sodium carbonate and the crude bromohydrin was collected. This was pulverized under water in a mortar, washed, and dried, affording 12.9 g (94%) of crude bromohydrin, mp 48–53°. Recrystallization from aqueous ethanol raised the melting point to 53–56° (lit.[12] 47°).

1,1-Diphenyl-2,3-dibromopropene-1 (4). The procedure of Pansevich-Kolyada[2] was essentially followed. A solution of 23 g of 1,1-diphenyl-2-bromopropanol-1 and 13.5 g of bromine in 120 ml of chloroform was irradiated at 350 mμ for 2.5 hr. At the end of this time, after much evolution of hydrogen bromide, the solution was pale yellow in color. The reaction mixture was washed with water, aqueous sodium carbonate, and aqueous sodium chloride, then dried and evaporated to yield 26.3 g (95%) of crude dibromide, mp 74–78°. Recrystallization from ethanol raised the melting point to 87–89° (lit.[2] 88–89°); nmr ($CDCl_3$) doublet at τ 2.9, singlet at 5.79, area ratio 10:2.1.

Anal. Calcd for $C_{15}H_{12}Br_2$: C, 51.17; H, 3.44; Br, 45.40. Found: C, 50.97; H, 3.27; Br, 45.70.

2-Bromo-3,3-(diphenylallyl)triphenylphosphonium Bromide (5). A solution of 49 g of 1,1-diphenyl-2,3-dibromopropene-1 and 27.5 g of triphenylphosphine in 450 ml of benzene was refluxed 3 hr. There was collected 82 g (96%) of salt **5**: mp 148–154°; nmr (CD_3CN) multiplets at τ 2.4 and 2.8, a weak peak at 3.4, and a doublet (*J* = 14 cps) at 5.1.

A small amount of **5** was converted to the corresponding perchlorate with aqueous sodium perchlorate. This material had mp 222–224° (from acetone–ether); nmr ($CDCl_3$) multiplets from τ to 2.2 to 3.6 and a doublet (*J* = 14 cps) at 5.2, peak area ratio 2.5:1.8.

Anal. Calcd for $C_{33}H_{27}BrClO_4P$: C, 62.52; H, 4.29; Br, 12.61; P, 4.89. Found: C, 62.72; H, 4.38; Br, 12.57; P, 4.89.

(3,3-Diphenylpropadienyl)triphenylphosphonium Bromide (6). Salt **5**, 6 g, was heated in 8 ml of diglyme for about 2 min. There was collected 4.2 g (81%) of crude salt **6**, mp 231–235°. Recrystallization from acetonitrile–ethyl acetate gave material with mp 233–235°; ir ($CHCl_3$) allene absorption at 5.21 μ; nmr ($CDCl_3$) doublet (*J* = 9 cps) at τ 1.3, multiplets at 2.4, 2.9, 3.2, peak area ratio 1.2:25.

Anal. Calcd for $C_{33}H_{26}BrP$: C, 74.30; H, 4.91; Br, 14.98; P, 5.81. Found: C, 74.21; H, 4.88; Br, 15.00; P, 5.82.

To a solution of 1 g of salt **5** in 10 ml of acetonitrile was added 0.2 ml of triethylamine. The solution was heated about 3 min and then allowed to cool. The collected solid was washed with water and dried. There was obtained 530 mg (72%) of salt **6**, ir absorption spectrum identical with that obtained above.

A small amount of **6** was converted to the perchlorate with aqueous sodium perchlorate. Recrystallization from acetonitrile–ethyl acetate afforded white needles, mp 193–194°; ir ($CHCl_3$) 3.0 (w), 3.42 (q), 4.10 (w), 5.20 (m), 6.32 (w), 6.76 (m), 6.98 (s), 7.493 (w), 9.01 (s), 9.34 (m), 9.77 (w), 10.05 μ (m); nmr ($CDCl_3$) multiplets from τ 2.3 to 3.3.

Anal. Calcd for $C_{33}H_{26}ClO_4P$: C, 71.67; H, 4.74; Cl, 6.41; P, 5.60. Found: C, 71.64; H, 4.81; Cl, 6.23; P, 5.77.

Treatment of 6 with Methanol. A solution of 250 mg of salt **6**, mp 231–233°, was refluxed 0.5 hr in methanol. The recovered material had mp 224–227°; ir spectrum essentially identical with that of starting material.

Treatment of 6 with *t*-Butyl Mercaptan. A small amount of salt **6** was heated for 5 min with excess *t*-butyl mercaptan in benzene. The ir spectrum of the recovered material showed no change. The reaction was repeated in methanol. Again, only unchanged **6** was recovered.

Addition of Aniline to 6. A suspension of 2.53 g of salt **6** in 35 ml of benzene was treated with 5 ml of aniline. The mixture was heated until homogeneous and then cooled. There was collected 3.1 g (100%) of the salt, mp 166–169°. Recrystallization from aqueous methanol gave material with mp 211–214°, apparently complexed with methanol. After heating at 58° (2 mm) for 2 hr the melting point was 209–213°; nmr multiplet at τ 2.0–3.5 (30), doublet (*J* = 14 cps) at 5.4 (1.8), singlet at 6.7 (<1). Material heated for 66 hr exhibited a considerably different nmr spectrum: multiplet at τ 2.3–3.6 (30), singlet at 3.8 (0.5), singlets at 5.00, 5.24, and 5.45 (1.6 total). The melting point was now 206–209°.

Anal. Calcd for $C_{39}H_{33}BrNP$: C, 74.76; H, 5.31; N, 2.24; P, 4.94. Found: C, 74.86; H, 5.44; N, 2.22; P, 4.89.

The crude bromide was converted to the perchlorate by treatment of a methanolic solution with aqueous sodium perchlorate. This material had mp 203–205°. Recrystallization from aqueous methanol raised the melting point to 212–214°. The nmr spectrum exhibited a multiplet at τ 2.3–3.6 (30), a broad singlet at 4.2 (0.8), and peaks at 5.05, 5.10, 5.22, 5.46, and 5.71 (1.9 total).

Anal. Calcd for $C_{39}H_{33}ClN_7OP$: C, 72.49; H, 5.15; Cl, 5.49; N, 2.18; P, 4.79. Found: C, 72.33; H, 5.14; Cl, 5.44; N, 2.19; P, 4.82.

Treatment of Aniline Adduct (7 or 8) with Aqueous Base. The aniline adduct of **6**, 0.2 g, was dissolved in methylene chloride and washed with dilute aqueous sodium hydroxide. The solution was dried and evaporated. The ir spectrum of the residue exhibited strong peaks at 5.18 and 11.70 μ.[13] The material was leached with pentane and the residue shown (by ir analysis) to be crude triphenylphosphine oxide.

The aniline adduct of **6**, 0.2 g, was dissolved in 10 ml of acetone and treated with dilute aqueous sodium carbonate. The solution was diluted with water and extracted with benzene. The extracts were dried and evaporated; the ir spectrum of the residue was essentially the same as that obtained above (aqueous sodium hydroxide treatment).

Treatment of Salt (7 or 8) with Phenyllithium. A slurry of 1.0 g of salt in 50 ml of ether was treated with phenyllithium solution until a brown color persisted. Excess phenyllithium was destroyed with water and the organic solution was washed, dried, and evaporated to a yellow oil. Hexane trituration caused crystallization to occur; there was collected 626 mg (72%) of crude ylide **12**, mp 142–150°. Recrystallization from benzene–hexane and methyl cyclohexane raised the melting point to 154–156°; ir 6.57 (s), 7.25 (s), 9.07 μ (s); nmr multiplet at τ 2.1–3.2 (34), "quartet" at 3.85 (2.6), doublet (*J* = 4 cps) at 4.8 (1.1).

Anal. Calcd for $C_{39}H_{32}NP$: C, 85.84; H, 5.91; N, 2.57; P, 5.68. Found: C, 85.93; H, 6.03; N, 2.45; P, 5.68.

Reaction of 12 with 3,4-Dichlorobenzaldehyde. To a solution of 3.4 g of ylide **12** in 25 ml of benzene was added 1.20 g of 3,4-dichlorobenzaldehyde in 10 ml of benzene. The mixture was refluxed 0.5 hr and evaporated to a yellow oil. Leaching with pentane

---

[10] All melting points are uncorrected. The nmr and ir spectra were determined on a Varian A-60 and Beckman IR5A.

[11] C. Hill and H. Bauer, *Chem. Ber.*, 37, 231 (1904).

[12] V. I. Pansevich-Kolyada and N. A. Prilizhoav, *J. Gen. Chem. USSR*, 21, 571 (1951).

[13] Diphenylallene is reported to exhibit strong peaks at 5.19 μ and 11.70 μ; W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Amer. Chem. Soc.*, 85, 2754 (1963).

left 1.4 g (75%) of triphenylphosphine oxide. The pentane solution was evaporated. The residue, 2.9 g of orange oil, exhibited a small peak at 4.71 μ in the ir; there was a strong pyridine-like odor apparent. The oil was taken up in benzene and treated with anhydrous hydrogen chloride. Solvent was evaporated and the residue was washed with cold methanol. There remained 1.5 g (52%) of crude **14**, mp 175°. Recrystallization from ethyl acetate raised the melting point to 185–189°; ir NH peak at 2.96 μ, strongest peak at 6.26 μ; nmr multiplet at τ 2.5–3.4 (20) and a broad singlet at 4.7 (0.8).

Anal. Calcd for $C_{28}H_{21}Cl_2N$: C, 76.01; H, 4.79; Cl, 16.03; N, 3.17. Found: C, 76.65; H, 4.97; Cl, 15.68; N, 2.90.

Treatment of 5 with Pyridine. Salt **5**, 250 mg, was dissolved in 5 ml of pyridine. Evaporation of the pyridine resulted in recovery of the starting salt (ir spectrum superimposable on that of starting material).

1,1-Diphenyl-4-*p*-nitrophenylbutatriene (16a). To a cold solution of 0.9 ml of triethylamine in 20 ml of acetonitrile was added 2 g of salt **5**. After 5 min 492 mg of *p*-nitrobenzaldehyde was added. The mixture was allowed to stand at room temperature for several minutes and was then diluted with aqueous methanol. There was collected 1.3 g (69%) of cumulene **16a**. Recrystallization from ethyl acetate afforded orange needles: mp 136–137°; ir ($CHCl_3$) 4.92 μ (m), 6.32 (s), 6.67 (s), 7.51 (s), 8.56 (m), 9.06 (s), 12.68 μ (s); nmr ($CDCl_3$) doublet at τ 2.0, multiplet at 2.6, singlet at 3.64, area ratio 2.1:12.0:0.9.

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31. Found: C, 80.95; H, 4.67, N, 4.42.

To a solution of 250 mg of salt **6**, the allenylphosphonium bromide, in 5 ml of pyridine was added 77 mg of *p*-nitrobenzaldehyde. The mixture was heated 5 min on the steam bath and then diluted with aqueous methanol. There was collected 93 mg (61%) of **16a**, mp 129–132°, mmp (with **16a** prepared from salt **5**) 130–135°.

1,1-Diphenyl-4-(3,4-dichlorophenyl)butatriene (16b). To a cold solution of 0.9 ml of triethylamine in 20 ml of acetonitrile was added 2 g of salt **5**. After 5 min 570 mg of 3,4-dichlorobenzaldehyde was added. The mixture was allowed to come to room temperature and was diluted with aqueous methanol. There was collected 1.1 g of yellow needles, mp 109–111°. Recrystallization from ethyl acetate afforded material with mp 113° dec; ir ($CHCl_3$) 4.94 (w), 6.36 (s), 7.20 (m), 8.88 (s), 9.76 (s), 11.38 (s), 12.12 μ (s); nmr ($CDCl_3$) multiplet at τ 2.7, singlet at 3.71, area ratio 13:1.

Anal. Calcd for $C_{22}H_{14}Cl_2$: C, 75.66; H, 4.04; Cl, 20.30. Found: C, 75.97; H, 4.04; Cl, 20.05.

N-Methyl-4,4-diphenyl-2,3-butadieneamide (18). To a solution of 2 g of salt **5** and 0.25 ml of methyl isocyanate in 15 ml of aceonitrile was added 0.7 ml of triethylamine. The mixture was heated 10 min and diluted with water. There was collected 230 mg (28%) of crude allenamide **18**, mp 189–191°. Repeat recrystallization from chloroform–hexane raised the melting point to 192–193°; ir ($CHCl_3$) 2.96 (w), 3.39 (w), 5.21 (w), 6.06 (s), 6.65 μ (m); nmr ($CDCl_3$) singlet at τ 2.76, singlet at 3.98, broad peak at 4.2, doublet at 7.2 (J = 4.5 cps) area ratios 10:1:0.8:3.

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.72; H, 6.24; N, 5.79.

The nmr spectrum in pyridine at 100° and chlorobenzene at 130° continued to exhibit the doublet at τ 7.2; there was no coalescence of the peaks.

Treatment of 5 with Diphenylketene. To a mixture of 2 g of **5** in 15 ml of acetonitrile was added 682 mg of diphenylketene prepared by the method of Staudinger.[14] The solution was cooled to 0° and then 1.5 ml of triethylamine was added. The mixture was was stirred 10 min at 0° and refluxed 5 min. It was then diluted with water and extracted with benzene. The extracts were washed, dried, evaporated, and chromatographed on silica gel and alumina. There was obtained 222 mg (19%) of crude hydrocarbon, mp 205–240°. Recrystallization from benzene–hexane and benzene–methanol raised the melting point to 260–262°; uv 296 (log ε 4.56), 370 mμ (log ε 3.77). The lit. values[8] are mp 260–262°; uv 297 (log ε 4.88), 385 mμ (log ε 3.77).

Anal. Calcd for $C_{58}H_{40}$: C, 94.53; H, 5.47; mol wt, 737. Found: C, 94.44; H, 5.46; mol wt, 730.

---

(14) H. Staudinger, *Chem. Ber.*, 38, 1735 (1905).

Formation of Pyridinium Ylides and Condensation with Aldehydes

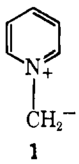
K. W. Ratts, R. K. Howe, and W. G. Phillips

Contribution from the Monsanto Company, Agricultural Division,
Research Department, St. Louis, Missouri 63166. *Received May 10, 1969*

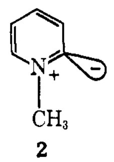
Abstract: Deuterium-exchange studies of N-methylpyridinium salts indicate that the 2 and 6 ring protons exchange more rapidly than the N-methyl protons under basic conditions which give no detectable exchange of the 3, 4, and 5 ring protons. However, under the same conditions condensation of these salts with aldehydes occurs exclusively at the N-methyl position. Discussion of these results is given in terms of formation of intermediate ylides **1** and **2**. Formation of either ylide **1** or **2** by decarboxylative methods in the presence of aldehydes leads to direct condensation to give N-(2-hydroxy-2-arylethyl)pyridinium and 2-(α-hydroxybenzyl)-N-methylpyridinium salts, respectively. These and other data are discussed and the conclusion drawn that the rate ratio of condensation to reprotonation is greater for ylide **1** than for ylide **2**.

The reaction of ylides with aldehydes has proven to be an extremely useful synthetic tool for the preparation of olefins (P ylides) and epoxides (S ylides).[1] Consequently correlation and explanation of ylide reactivity is of considerable interest from the standpoint of synthetic utility.

Pyridinium ylides are of some significance since (1) there exists no possibility for d-orbital stabilization of the carbanion and (2) two possible ylide structures may form (**1** and **2**). Condensation of pyridinium ylides with aldehydes, contrary to known reactions of P or S ylides, produces the corresponding alcohols.[2–4]



1



2

---

(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1967.

(2) R. K. Howe and K. W. Ratts, *Tetrahedron Letters*, 4743 (1967); (b) W. G. Phillips and K. W. Ratts, *ibid.*, 1383 (1969).

(3) M. R. F. Ashworth, R. P. Daffern, and D. L. Hammick, *J. Chem. Soc.*, 809 (1939).

(4) F. Krohnke, *Angew. Chem.*, 65, 605 (1953).