Reactions of Phosphorus Compounds. 37. Preparation of β-Iminopropyl- and β-Aminopropenyltriphenylphosphonium Bromides and the Use of the Latter in Heterocyclic Synthesis

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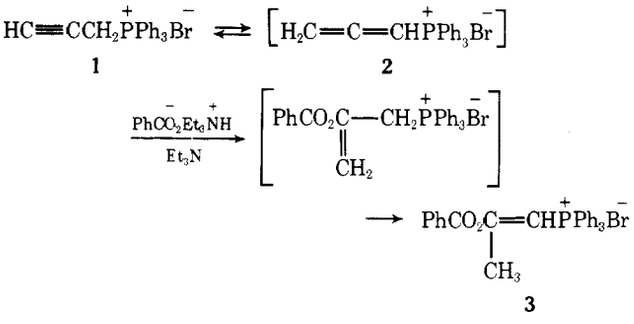
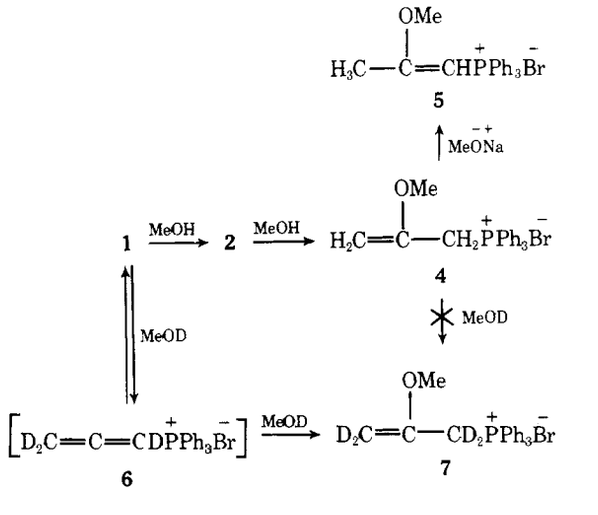
Support is given for the initial isomerization of prop-2-ynyltriphenylphosphonium bromide (1) to propadienyltriphenylphosphonium bromide (2) prior to the addition of nucleophiles to form substituted phosphonium salts. By ^{31}P NMR the 22 salts formed by the nucleophilic addition of primary amines to 2 were found to be in either the enamine or imine configuration. Synthesis of a number of substituted quinolines, 10, was accomplished by intramolecular Wittig reactions of the corresponding adducts, 8. Prop-1-ynyltriphenylphosphonium bromide was also prepared.

In 1965 Eiter and Oediger[1] reported the preparation of prop-2-ynyltriphenylphosphonium bromide (1) and its use in the Wittig reaction. The addition reactions of nucleophiles to prop-2-ynyl phenyl sulfones,[2] prop-2-ynyldialkylsulfonium salts,[3] and the corresponding sulfides[4] have been shown to be successful owing to an initial isomerization of the 2-alkynyl moiety to an allenyl species. Appleyard and Stirling only postulated[2] that the benzoate anion added to the allenyltriphenylphosphonium bromide (2) on going from 1 to the benzoate ester of 2-hydroxypropenyltriphenylphosphonium bromide (3). It has been shown conclusively in our laboratories



that 2 is the intermediate in conjugate additions of nucleophiles to 1.

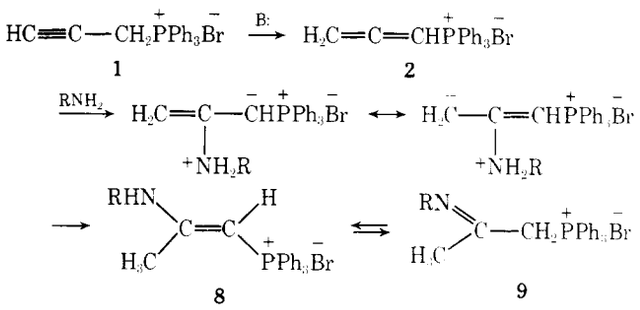
Methanol, as well as other alcohols, has been shown to add readily to 1, after an initiation period of approximately 2 h, under refluxing conditions, to give the 2-methoxyallyltriphenylphosphonium bromide (4). When a catalytic amount of base was added to the initial reaction mixture, or to a methanolic solution of 4, the 2-methoxypropenyltriphenylphosphonium bromide, 5, was formed rapidly. The reaction of deuteriomethanol with 1 gave 7. However, treatment of 4 with deuteriomethanol did not give 7, thus showing that the incorporation of deuterium into the molecule must have occurred during the conversion of 1 to the 1,3,3-trideuterioallenyltriphenylphosphonium bromide, 6, prior to the conjugate addition of methanol. The intermediacy of the allenyl salt, 2 (or 6), was thus shown.



Isolation of 2 was accomplished by treatment of 1 in *tert*-butyl alcohol with a catalytic amount of potassium *tert*-butylate.[5] The preparation of prop-1-ynyltriphenylphosphonium bromide was accomplished by heating 1 with phenol.

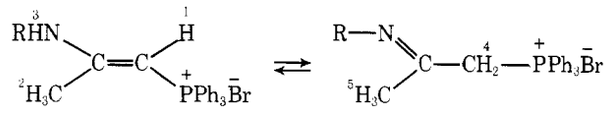
The mechanism of the nucleophilic addition of primary amines to the propargyl salt (1) is undoubtedly analogous to the addition of primary alcohols to 1 and is shown in Scheme I. We have added a large number of amines to salt 1. The yields

Scheme I

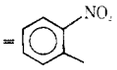
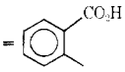
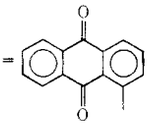
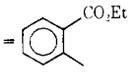
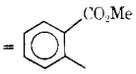
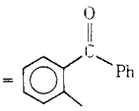
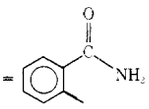
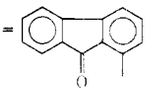
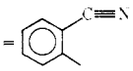
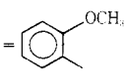
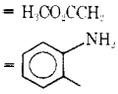
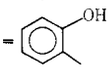
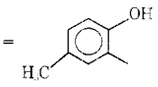
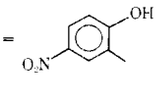


and physical data (^1H NMR, ^{31}P NMR, and IR spectra) for the phosphonium salts are given in Tables I, II, III, and IV, respectively. We have shown previously, by ^{13}C NMR,[6] that the stereochemistry about the carbon–carbon double bond in 8 was uniquely determined as the *E* form as shown. The ^1H NMR of the phosphonium salts showed either a methylene, for 9, at δ 4.80–5.65 ppm (d, 2, J_{PH} = 14.0–14.9 Hz) or a vinyl proton, for 8, at δ 3.75–5.10 ppm (d, 1, J_{PH} = 12.7–15.0 Hz) or, as in the case of 8E–9E, both, thus indicating the presence of an enamine–imine equilibrium. From the observed ^{31}P chemical shifts and the relative peak areas for each salt (A–V), we assigned the compound the structure 8 or 9 and calculated the percent composition ratio (8:9) as given in Table III. Further examination of the ^{31}P NMR data revealed two distinct ranges of chemical shifts (1) δ 12.9–18.6 ppm for the enamines or (2) δ 20.3–22.5 ppm for the imines, which is in agreement with our assignments of structure for the phosphonium salts 9A–8V. The assignment of the ^{31}P chemical shifts for the enamine or imine structure is supported by previous work[7,8] emanating from these laboratories.

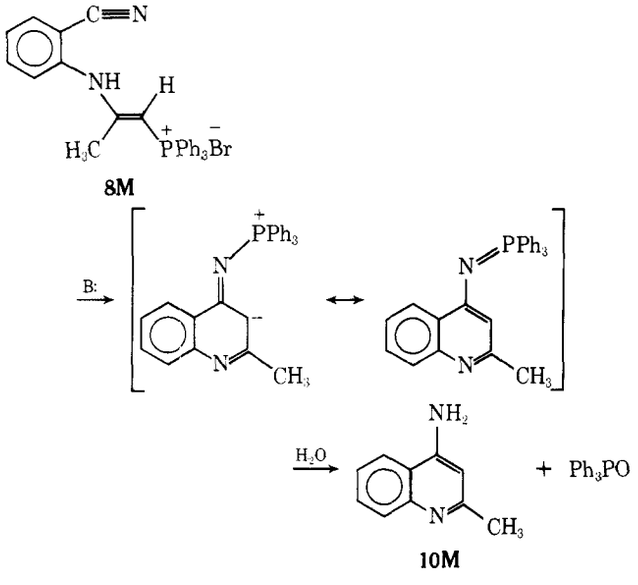
Table I



8 9

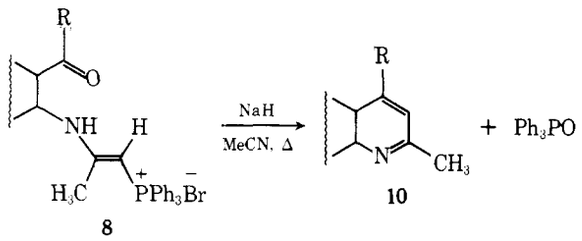
Salt	Mp, °C	% yield	Anal. Calcd C	Anal. Calcd H	Anal. Calcd N	Anal. Found C	Anal. Found H	Anal. Found N
9A R = Ph—C(=O)—NH—	259–260	86	65.00	5.06		64.78	4.98	
9B R = O$_2$N(NO$_2$)C$_6$H$_3$—NH—	238	81	55.96	4.17		55.95	4.11	
9C R = O$_2$N(H)C$_6$H$_3$—NH—	233	81	60.68	4.71	7.86	60.46	4.57	7.33
9D R = Ph—NH—	208	60.5	66.26	5.35	5.72	66.71	5.63	5.42
9E R = 	207	92.5	62.44	4.66	5.39	62.35	4.79	5.39
8F R = 	221–222	70	64.87	4.86	2.70	64.72	4.91	2.63
8G R = 	206–207	10.9	69.54	4.50	2.31	69.35	4.74	2.19
8H R = 	159.5–160	74	65.94	5.34		65.75	5.20	
8I R = 	182–184	92	65.40	5.11		65.16	5.05	
8J R = 	220–221	95	70.58	5.04		70.41	5.28	
8K R = 	215–215.5	40	64.17	5.18		64.33	4.79	
8L R = 	231	81.6	70.84	4.72	2.43	70.65	5.25	2.35
8M R = 	245	60.5	67.34	4.84	5.61	67.45	4.86	5.36
8N R = HO$_2$C—C$_6$H$_4$—	281–282	78.2	64.87	4.86	2.70	64.37	4.68	2.53
8O R = H$_3$C—C(=O)—C$_6$H$_4$—	218–219	40	67.45	5.27	2.71	67.39	5.24	2.43
8P R = Ph	262–263	88	66.35	5.31		68.34	5.50	
8Q R = 	212	94	66.67	5.39	2.78	66.68	5.42	2.53
8R R = H$_3$CO$_2$CCH$_2$	209	31	61.29	5.36	2.97	61.70	5.42	2.82
8S R = 	241–242	59	66.26	5.35	5.72	66.51	5.27	5.45
8T R = 	230–231	92	66.12	5.15	2.85	66.89	5.29	2.88
8U R = 	224	51	66.67	5.39	2.78	66.78	5.33	2.84
8V R = 	233–234	62	60.57	4.52	5.23	60.12	4.69	5.10

Synthesis of heterocyclic compounds via the Wittig reaction has been reviewed recently by Zbiral.[9] Our major interest in this work was the use of the phosphonium salts prepared above, substituted in such a manner to allow for an intramolecular Wittig reaction with a carbonyl (or nitrile) moiety, for the synthesis of heterocyclic species. We have previously shown[10] that upon treatment with base, several substituted salts, **8I** and **8J**, undergo an intramolecular Wittig reaction yielding substituted quinolines. We have further extended the application of this particular intramolecular Wittig reaction to include the synthesis of a simple quinoline (**10M**) by the



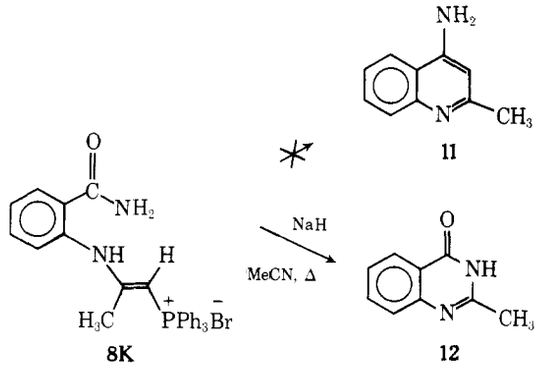
8M **10M**

attack of the ylide on a carbon–nitrogen triple bond[11] and the synthesis of tetracyclic quinolines (**10G, 10L**). The physical (see Table V) and spectral data support the structures of the isolated products **10**.



8 **10**

Treatment of the esters **8H** and **8I** yields vinyl ethers, an abnormal pathway encountered previously.[12] Esters and ylides normally give β-ketophosphonium ylides;[13-15] therefore, one might anticipate that the amide, **8K**, would yield a vinyl



8K **11** **12**

amine, 2-methyl-4-aminoquinoline (**11**). However, 2-methylquinazol-4-one (**12**), was obtained via an unusual methylenephosphorane extrusion process.[16] An examination of the methylenephosphorane extrusion reaction is under investigation.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer, ^1H NMR spectra on a Perkin-Elmer Model R12B spectrometer using tetramethylsilane as internal standard, and ^{31}P NMR spectra on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{31}P NMR data were taken at the operating frequency of 36.43 MHz. The ^{31}P chemical shifts are reported as referenced to external 85% H_3PO_4 with shifts occurring downfield from the reference taken as positive. All melting points were uncorrected and obtained on a Thomas-Hoover capillary melting point apparatus. Elemental analyses are by Micro Analysis Inc., Wilmington, Del., and MHW Laboratories, Garden City, Mich. Any analytical and spectral data not included in text may be found in the tables. All reactions were run under dry nitrogen using anhydrous solvents.

Triphenyl(prop-2-ynyl)phosphonium Bromide (1).[1] To a solution of 210 g (0.80 mol) of triphenylphosphine and 400 ml of 1,4-dioxane in a 1-l. Morton flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel, 90 ml of 48% HBr was added over a 30-min period. After the reaction mixture became homogeneous, 96 g (0.80 mol) of propargyl bromide was slowly added over a 90-min period. The reaction mixture was stirred for 3 h and filtered. Recrystallization with 2-propanol gave 230 g (75% yield) of **1** as white crystals: mp 179 °C dec (lit.[1] mp 156–158 °C); NMR (CF_3COOH) δ 2.3 (m, 1, J_{HH} = 2.8, J_{PH} = 6.5 Hz, C≡CH), 4.5 (dd, 2, J_{HH} = 2.8, J_{PH} = 15.0 Hz, $-CH_2P$); IR 1440, 1110 cm^{-1} (P–C).

Propadienyltriphenylphosphonium Bromide (2). A 3.8-g (0.01 mol) sample of **1** in 50 ml of dried Me_2SO was stirred with a catalytic amount of potassium *tert*-butylate for 2 h at room temperature under a nitrogen atmosphere. The deep red solution was precipitated by pouring it into 300 ml of ether. After two washings with ether, an orange solid, **2**, was obtained. The salt resisted recrystallization to give an analytical sample: IR ($CHCl_3$) 1960 (⟩C=C=C⟨), 1440 (C–P), 1115 cm^{-1} (P–phenyl), NMR ($CDCl_3$) δ 5.40 (dd, 2, J_{HH} = 6.5, J_{PH} = 13.0 Hz, H_2C=C=C⟨), 7.4–8.3 (m, 16, ⟩C=C=CHP and aromatic).

2-Methoxyprop-2-enyltriphenylphosphonium Bromide (4). To a 100-ml round-bottom flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet 10.0 g (0.026 mol) of **1**, 40 ml of dry $CHCl_3$, and 20 ml (large excess) of freshly distilled methanol were added. The reaction mixture was heated at reflux with stirring for a period of 4 h. The yellow solution was then allowed to cool to room temperature and concentrated on a rotary evaporator to a yellow oil. Addition of EtOAc produced a solid which yielded 10.03 g (97% yield) of a white solid, **4**: mp 142 °C after recrystallization from $CHCl_3$–EtOAc; IR 1610 (C=C), 1420 (C–P), 1280 (C–O–C), 1100 cm^{-1} (P–phenyl); NMr ⟩cdcl$_3$) δ 3.29 (s, 3, $-OCH_3$), 4.18 (dd, 1, J_{HH} = 2.5 ± 0.5 Hz, HC=C), 4.65 (dd, 1, J_{HH} = 2.5 ± 0.5 Hz, HC=C), 4.85 (d, 2, J_{PH} = 14 Hz, $-CH_2P$), 7.5–8.2 (m, 15, aromatic).

Anal. Calcd for $C_{22}H_{22}OPBr$: C, 63.78; H, 5.60. Found: C, 63.85; H, 5.69.

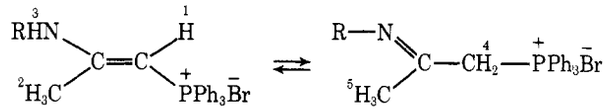
2-Methoxyprop-1-enyltriphenylphosphonium Bromide (5). To a 50-ml round-bottom flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet, 20 ml (large excess) of freshly distilled CH_3OH and a catalytic amount of sodium were added. After hydrogen evolution ceased, 3.80 g (0.01 mol) of **1** was added and the solution was heated at reflux for 10 min. The solution was then concentrated to an oil on a rotary evaporator and the oil poured slowly into 200 ml of EtOAc with stirring. A solid, **5**, separated which upon crystallization had mp 155 °C and weighed 3.73 g (90% yield): IR 1601 (C=C), 1420 (C–P), 1330 (C–O–C), 1110 cm^{-1} (P–phenyl); NMR δ 2.60 (s, 3, $-CH_3$), 3.68 (s, 3, $-OCH_3$), 5.68 (d, 1, J_{PH} = 17 Hz, =CHP), 7.4–8.0 (m, 15, aromatic).

Anal. Calcd for $C_{22}H_{22}OPBr$: C, 63.78; H, 5.60. Found: C, 63.89; H, 5.36.

2-Methoxy-1,1,3,3-tetradeuterioprop-2-enyltriphenylphosphonium Bromide (7). The salt **7** was prepared in the same manner as **4** above. Freshly distilled CH_3OD was substituted for the CH_3OH. The melting point and IR were essentially identical with those of **5**. The NMR ($CDCl_3$) showed δ 3.30 (s, 3, $-OCH_3$), 7.5–8.2 (m, 15, aromatic).

Prop-1-ynyltriphenylphosphonium Bromide. To a 100-ml flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet were added 10 g (0.026 mol) of **1**, 60 ml of CH_2Cl_2, and 2.50 g (equimolar amount) of phenol. The mixture was heated at reflux with stirring until all of the solid was dissolved. The solution was allowed to cool and the stirring was continued for 3 h. The mixture was then

Table II. ^{1}H NMR (δ)



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Salt	1	2	3	4	5	Aromatic	Other
9A				5.40 (d, 2, J_{PH} = 14.6 Hz)	2.20 (s, 3)	7.4–8.3 (m, 21)	CH_2 (d, 2, J = 13.4 Hz) 4.6; CH_3 (s, 3) 1.8; OH in aromatic region[a]
9B				5.40 (d, 2, J_{PH} = 14.5 Hz)	2.20 (s, 3)	7.5–8.1 (m, 18)	NH (d, 1, J = 2.66 Hz) 8.8
9C				5.30 (d, 2, J_{PH} = 14.9 Hz)	2.20 (s, 3)	7.5–8.2 (m, 19)	NH (s, 1) 10.3
9D				4.80 (d, 2, J_{PH} = 14.0 Hz)	2.15 (s, 3)	6.5–8.0 (m, 20)	NH (s, 1) 8.87
9E	4.25 (d, 1, J_{PH} = 13.3 Hz)	2.30 (s, 3)	10.6 (bs, 1)	5.65 (d, 2, J_{PH} = 12.0 Hz)	2.3 (d, 3, J = 2.6 Hz)	7.5–8.3 (m, 19)	
8F	4.4 (d, 1, J_{PH} = 14.7 Hz)	1.85 (s, 3)	10.1 (bs, 1)			7.1–8.2 (m, 19)	
8G	5.03 (d, 1, J_{PH} = 13.4 Hz)	2.03 (s, 3)	10.6 (bs, 1)			7.0–7.8 (m, 22)	
8H	4.55 (d, 1, J_{PH} = 14.3 Hz)	2.0 (s, 3)	10.3 bs, 1)			7.0–8.2 (m, 19)	CH_2 (q, 2, J = 7.0 Hz) 4.3; CH_3 (t, 3, J = 7.0 Hz) 1.3
8I	4.5 (d, 1, J_{PH} = 14.74 Hz)	2.05 (s, 3)				6.95–8.3 (m, 19)	$-\overset{O}{\overset{\|}{C}}-CH_3$ (s, 3) 3.85
8J	4.20 (d, 1, J_{PH} = 15.0 Hz)	1.75 (s, 3)				7.2–8.2 (m, 24)	
8K	4.40 (d, 1, J_{PH} = 14.5 Hz)	1.80 (s, 3)	10.13 (bs, 1)			7.4–8.2 (m, 19)	NH_2 (s, 2) 8.5
8L	4.50 (d, 1, J_{PH} = 13.4 Hz)	2.00 (s, 3)	10.2 (bs, 1)			7.1–7.9 (m, 22)	
8M	4.15 (d, 1, J_{PH} = 13.5 Hz)	2.00 (s, 3)	10.7 (bs, 1)			7.3–7.9 (m, 19)	
8N	5.10 (d, 1, J_{PH} = 14.9 Hz)	1.85 (s, 3)	10.15 (bs, 1)			7.5–8.1 (m, 19)	OH in aromatic region
8O	5.08 (d, 1, J_{PH} = 14.9 Hz)	1.95 (s, 3)	10.3 (bs, 1)			7.5–8.1 (m, 19)	$-\overset{O}{\overset{\|}{C}}-CH_3$ (s, 3) 2.55
8P	4.75 (d, 1, J_{PH} = 15.0 Hz)	2.05 (s, 3)	10.50 (bs, 1)			7.2–7.8 (m, 20)	
8Q	4.15 (d, 1, J_{PH} = 14.7 Hz)	2.00 (s, 3)	9.8 (bs, 1)			6.9–7.7 (m, 19)	$-OCH_3$ (s, 3) 3.8
8R	3.75 (d, 1, J_{PH} = 12.7 Hz)	1.90 (s, 3)	9.0 (bs, 1)			7.5–7.9 (m, 15)	CH_2 (d, 2, J_{PH} = 6.0 Hz) 4.2; OCH_3 (s, 3) 3.73
8S	3.95 (d, 1, J_{PH} = 14.7 Hz)	1.85 (s, 3)	9.5 (bs, 1)			6.5–8.0 (m, 19)	NH_2 (s, 2) 5.4
8T	4.15 (d, 1, J_{PH} = 14.7 Hz)	1.85 (s, 3)	9.5 (bs, 1)			6.75–8.0 (m, 20)	OH in aromatic region
8U	4.10 (d, 1, J_{PH} = 15.3 Hz)	1.80 (s, 3)	9.6 (bs, 1)			6.9–8.0 (m, 19)	CH_3 (s, 3) 2.2
8V	4.30 (d, 1, J_{PH} = 13.3 Hz)	1.85 (s, 3)	10.0 (bs, 1)			7.25–8.35 (m, 19)	OH in aromatic region

[a] See footnote *a*, Table III.

poured slowly with stirring into 200 ml of EtOAc. Stirring was continued until a white solid was produced. The solid was twice recrystallized from $CHCl_3$–EtOAc to give 8.5 g (85% yield) of prop-1-ynyltriphenylphosphonium bromide as white crystals. The salt appears to exist in two crystalline forms, one having mp 130 °C and the second mp 193 °C. Both forms give the same NMR and IR spectra. IR ($CHCl_3$) 2900 (C–H), 2200 (C≡C), 1440 (C–P), 1110 cm^{-1} (P–phenyl); NMR ($CDCl_3$) δ 2.75 (d, 3, J_{PH} = 5 Hz, $-CH_3$), 7.5–8.2 (m, 15, aromatic).

Anal. Calcd for $C_{21}H_{18}PBr$: C, 66.30; H, 4.76. Found: C, 66.35; H, 4.72.

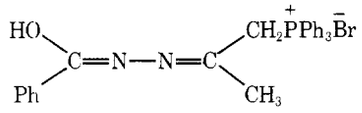
General Procedure for the Preparation of the β-Aminopropenyltriphenylphosphonium Bromides (9A–8V). Into a dry flask, fitted with a reflux condenser, gas inlet, and magnetic stirrer, were placed equimolar amounts (0.02 mol) of the amine, triphenyl(prop-2-ynyl)phosphonium bromide (1), and 200 ml of CH_3CN (dried and distilled over P_2O_5). The mixture was stirred and refluxed until TLC indicated the disappearance of the phosphonium salt, 1 (3 h to 3 days). After cooling, the mixture was concentrated to an oil, dissolved in a minimum amount of CH_2Cl_2, and added slowly with stirring to EtOAc. The solution was stirred for 0.5 h and then filtered. The product was recrystallized to a constant melting point in CH_2Cl_2–EtOAc. The results are shown in Table I.

General Procedure for the Preparation of Substituted Quinolines (10). Equimolar amounts of the phosphonium salt (9 or 8) and NaH (57% in mineral oil) were allowed to react in a 500-ml one-neck round-bottomed flask fitted with a reflux condenser and nitrogen inlet by dissolving the salt in dry CH_3CN and then adding the NaH which was washed three times with hexane. More CH_3CN was added so that the total volume was 250 ml. The reaction mixture was refluxed and stirred under nitrogen for 3 days. After cooling, the mixture was filtered and poured into water. The water layer was extracted three times with ether, made basic with KOH, and extracted two more times with ether. The combined ether layers were dried (K_2CO_3), filtered, and concentrated to an oil (crude product 10) with a rotary evaporator. The workup is described below.

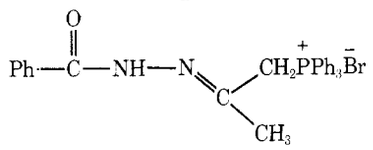
Table III. ^{31}P NMR (δ)

Salt	%8:%9	δ 8, ppm	δ 9, ppm
9A	0:100[a]		(19.1) 20.2
9B	0:100		21.0
9C	0:100		21.1
9D	0:100		21.8
9E	1:2	16.3	21.2
8F	6:1	15.6	22.2
8G	5:1	15.6	22.0
8H	5:1	16.7	22.5
8I	3:1	16.4	22.0
8J	3:1	12.9	20.3
8K	>99:trace	15.9	21.8
8L	>99:trace	16.1	21.6
8M	>99:trace	16.4	21.3
8N	>99:trace	15.4	21.5
8O	100:0	16.8	
8P	100:0	16.8	
8Q	100:0	16.4	
8R	100:0	16.0	
8S	100:0	15.5	
8T	100:0	15.3	
8U	100:0	15.4	
8V	100:0	18.6	

[a] 9A has structures a and b in a 1:1 ratio. [b] The chemical



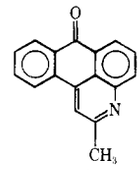
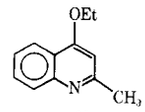
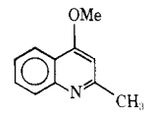
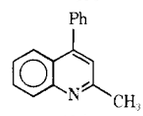
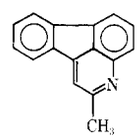
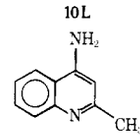
a



b

shifts are referenced to external 85% H_3PO_4 with shifts occurring downfield from the reference taken as positive. All samples were run at 28 °C with broad band ^1H decoupling.

Table V. Quinoline Derivatives

	Mp, °C	% yield	m/e Theory	m/e Exptl
 10G	190	41.2	245.0840	245.0840
 10H	48	59.5	187.0997	187.0956
 10I	63–65	53		
 10J	96.5–98	64	219.1048	219.1034
 10L	135	42	217.0891	217.0906
 10M	167–169	31		

2-Methyldibenz[*f,i,j*]isoquinol-7-one (10G). The oil obtained from treating compound **8G** by the general procedure was placed on a silica gel column and eluted with EtOAc to remove unreacted starting material. The resulting oil was dissolved in 95% EtOH and added to an equal volume of picric acid in 95% EtOH (saturated). The yellow crystals, picrate derivative of **10G**, were collected and recrystallized in 95% EtOH. The picrate salt was then dissolved in a minimal amount of EtOH, placed on an alumina column, and eluted with petroleum ether. Concentration of the fractions yields the desired product **10G**: mp 190 °C; NMR ($CDCl_3$) δ 2.9 (s, 3, $-CH_3$), 7.3–8.8 (m, 8, aromatic).

4-Ethoxy-2-methylquinoline (10H). The oil obtained from treating compound **8H** by the general procedure was purified in the

Table IV. Major Infrared Absorption Bands (cm^{-1})

Salt	P–Ph	P–C	N–H	Olefin	>C=N	>C=O	Other
9A	1100		2900		1600		
9B	1100	1430	3200		1650		1525 d, 1430 d
9C	1105	1440	2900, 3100		1600		1490
9D	1100	1440	3000		1590		
9E	1110	1440	3000		1580		1540
8F	1100	1440	3200	1600		1725	1260
8G	1090	1420	3000	1525		1680	1260, 1310
8H	1110	1440	3000	1530		1720	1240, 1290
8I	1110	1430	3400	1650		1700	1290
8J	1110	1440				1750	
8K	1110	1420	3000–3600	1560		1680	
8L	1110	1440	3050	1600		1700	
8M	1110	1430	3000	1580			2250
8N	1085					1680	
8O	1090	1440	2900	1550		1660	
8P	1110	1440					1220
8Q	1100	1410	2900	1550			1260
8R	1100	1440	3100, 3300	1550		1780	1200
8S	1090	1440	3300	1550			1590, 990
8T	1100	1420	3300	1500			3200
8U	1110	1430	3200	1500			1580
8V	1100	1420	3400	1490			1575

same manner as **10G** above to yield the desired product **10H:** mp 48 °C; NMR ($CDCl_3$) δ 1.5 (t, 3, J_{HH} = 11.3 Hz, $-CH_2CH_3$), 2.6 (s, 3, $-CH_3$), 4.15 (q, 2, J_{HH} = 11.3 Hz, $-CH_2CH_3$), 6.5 (s, 1, 3-aromatic proton), 7.2–8.3 (m, 4, aromatic).

2-Methyl-4-methoxyquinoline (10I). The oil obtained from treating compound **8I** by the general procedure was sublimed three times to give colorless crystals, 0.23 g (30% yield) of **10I.** A 53% yield of Ph_3PO, mp 150–153 °C, was found; **10I** had mp 63–65 °C (lit.[17] mp 58–59 °C).

2-Methyl-4-phenylquinoline (10J). The oil obtained from treating compound **8J** by the general procedure was sublimed at 80 °C under vacuum. The material left after sublimation was impure Ph_3PO in 90% yield. The sublimate weighed 0.55 g (64% yield), slightly yellow needles, **10J,** mp 96.5–98 °C (lit.[18] mp 97–98 °C).

2-Methylindeno[1,2,3-*de*]quinoline (10L). The oil obtained from treating compound **8L** by the general procedure was purified in the same manner as **10G** to yield the desired product **10L:** mp 135 °C dec; NMR ($CDCl_3$) δ 2.8 (s, 3, $-CH_3$), 7.2–8.0 (m, 8, aromatic).

4-Amino-2-methylquinoline (10M). The oil obtained from treating compound **8M** by the general procedure was dissolved in CH_2Cl_2 and dripped slowly into hexane. The resulting precipitate was collected and recrystallized in benzene–hexane to yield 0.29 g (31% yield) of **10M,** mp 167–169 °C (lit.[19] mp 167–169 °C).

Registry No.—**1,** 2091-46-5; **2,** 54599-99-4; **4,** 60661-63-4; **5,** 60661-64-5; **7,** 60661-65-6; **8F,** 60661-66-7; **8G,** 60661-67-8; **8H,** 60661-68-9; **8I,** 60661-69-0; **8J,** 60661-70-3; **8K,** 60661-71-4; **8L,** 60661-72-5; **8M,** 60661-73-6; **8N,** 60661-74-7; **8O,** 60661-75-8; **8P,** 54774-75-3; **8Q,** 60661-76-9; **8R,** 54774-76-4; **8S,** 60661-77-0; **8T,** 60661-78-1; **8U,** 60661-79-2; **8V,** 60661-80-5; **9A** (keto form), 60661-81-6; **9B,** 60661-82-7; **9C,** 60661-83-8; **9D,** 54774-78-6; **9E,** 60661-84-9; **10G,** 60661-85-0; **10H,** 46272-56-4; **10I,** 31835-53-7; **10J,** 1721-92-2; **10L,** 60661-86-1; **10M,** 6628-04-2; triphenylphosphine, 603-35-0; propargyl bromide, 106-96-7; methanol, 67-56-1; CH_3OD. 1455-13-6; prop-1-ynyltriphenylphosphonium bromide, 54599-98-3; benzoic acid hydrazide, 613-94-5; 2,4-dinitrophenylhydrazine, 119-26-6; 4-nitrophinylhydrazine, 100-16-3; phenylhydrazine, 100-63-0; 2-nitrobenzenamine, 88-74-4; 2-aminobenzoic acid, 118-92-3; 1-amino-9,10-anthracenedione, 82-45-1; ethyl 2-aminobenzoate, 87-25-2; methyl 2-aminobenzoate, 134-20-3; (2-aminophenyl)phenylmethanone, 2835-77-0; 2-aminobenzamide, 88-68-6; 1-amino-9*H*-fluoren-9-one, 6344-62-3; 2-aminobenzonitrile, 1885-29-6; 4-aminobenzoic acid, 150-13-0; 1-(4-aminophenyl)ethanone, 99-92-3; benzenamine, 62-53-3; 2-methoxybenzenamine, 90-04-0; methyl glycinate, 616-34-2; 1,2-benzenediamine, 95-54-5; 2-aminophenol, 95-55-6; 2-amino-4-methylphenol, 95-84-1; 2-amino-4-nitrophenol, 99-57-0; triphenylphosphine oxide, 791-28-6; **9A** (enol form), 61484-35-3.

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The Effect of the Base Strength upon the Structure of the Transition State in E2 Reactions. Kinetics of Eliminations from 2-Arylethyltrimethylammonium Bromides Promoted by Sodium Phenoxide and Sodium *m*-Nitrophenoxide in *N,N*-Dimethylformamide

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Values of the Hammett constant, ρ, and deuterium kinetic isotope effect (k_H/k_D) have been determined for the eliminations from 2-arylethyltrimethylammonium bromides promoted by sodium phenoxide and sodium *m*-nitrophenoxide in *N,N*-dimethylformamide. These values indicate that the transition state of the reaction with sodium phenoxide has a carbanion character higher than that of the reaction with sodium *m*-nitrophenoxide. The phenomenon is mainly due to a significant decrease of C_α–leaving group bond stretching at the transition state of the reaction with the stronger base since the degree of C_β–H bond rupture in the reaction with sodium phenoxide is smaller than in the reaction with sodium *m*-nitrophenoxide. These results are compared with those obtained in the elimination from 2-arylethyl bromides and discussed in the light of recent theories concerning the effect of structural changes in the reactants on the transition state of E2 reactions.

The study of the effect of structural changes in the reactants on the structure of the transition state of E2 reactions is of great importance from both theoretical and practical points of view. Recently, on the basis of theoretical treatments, it has been shown that both parallel and perpendicular modes of vibration of the transition state can be affected by structural changes in the reactants.[1,2] The effects on the parallel modes (parallel effects) result in modifications of the structure of the transition state in agreement with the Hammond postulate;[3] those on the perpendicular modes (perpendicular effects) result in modifications in the opposite direction. As a further development of the theory, it has been also suggested that the relative weight of perpendicular and parallel effects can closely depend on the location of the transition state in the reaction