C, 65.11; H, 5.48; N, 1.83.

Based on these data, $RhCl(PPh_3)_2$(pyrrolidine) may be suggested as the structure of the crystals.

The same complex, which was identified by elemental analysis, IR spectrum, and melting point, was obtained in the similar reaction between $[RhCl(PPh_3)_2]_2$[8a] and pyrrolidine.

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Reactions of Phosphorus Compounds. 38. Methylenetriphenylphosphorane Extrusion Reaction

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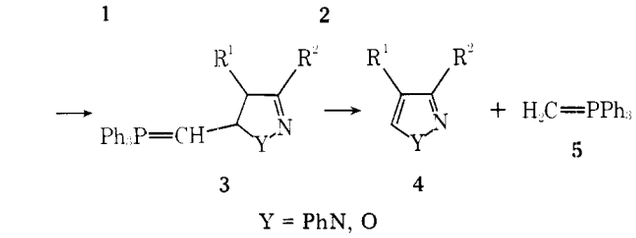
Received October 28, 1977

Synthesis of a number of heterocycles was accomplished by an ylide extrusion reaction. The effects of varying the heteroatoms and of substituting (2-phenylethynyl)- (**12**) for prop-2-ynyltriphenylphosphonium bromide (**11**) on the rate of the reaction were studied.

We have previously communicated, in this journal,[1] a generally useful synthetic process involving the elimination of methylenetriphenylphosphorane (**5**). In most of the reactions in which the elimination of methylenetriphenylphosphorane is postulated, the phosphorane cannot be isolated but appears to occur as an intermediate on the pathway to an observed product.[2-7] In a few cases, however, ylides may be observed as major reaction products.[8-10]



Examples of the latter are found during the formation of pyrazoles and isoxazoles (**4**)[9] or during the formation of a dithio lactone (**8**).[10]

The current work has centered on extending the scope of the methylenetriphenylphosphorane extrusion reaction of triphenyl(prop-2-ynyl)phosphonium bromide (**11**) and (2-phenylethynyl)triphenylphosphonium bromide (**12**). The preparation and structures of the intermediate (β-aminopropenyl)triphenylphosphonium bromides (**13**) have been discussed previously.[11] The yields of the heterocyclic species

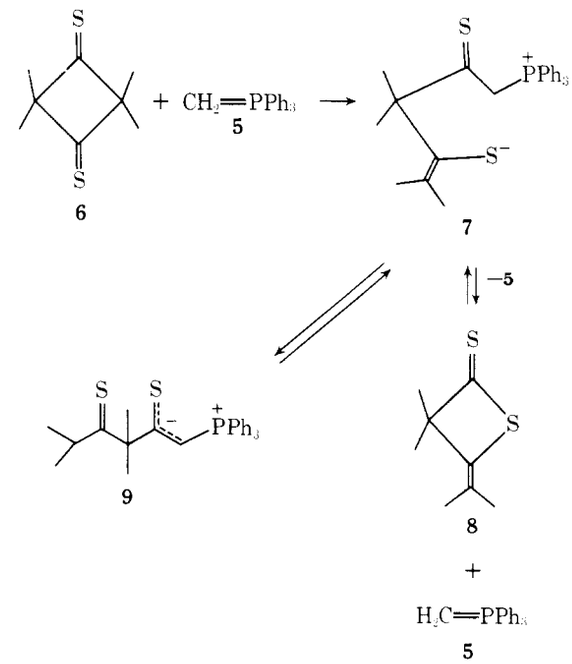


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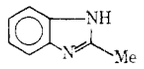
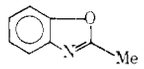
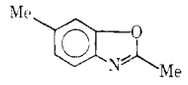
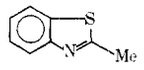
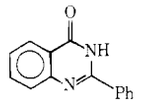
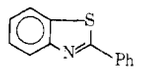
Table I. Heterocycles Prepared Via Methylenephosphorane Extrusion

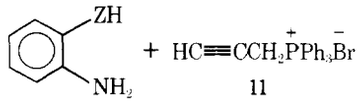
Compd	Registry no.	Mp/bp (mm), °C	Yield, %	Sadtler NMR reference
 14C	615-15-6	175–176 (lit.[16] 176–177)	83	7646
 14B	95-21-6	36 (0.5 mm) (lit.[17] 200–201)	50	17206
 14G	53012-61-6	74.5–76 (3 mm) (lit.[18] 218–219)	80	869
 14A	120-75-2	67 (1.2 mm) (lit.[19] 238)	62	Varian 191
 16E	1022-45-3	244–245 (lit.[13] 241)	45	^{1}H NMR (Me_2SO-d_6) δ 7.2–8.4 (m, 10)
 16A	883-93-2	113.5–114 (lit.[14] 115)	53	^{1}H NMR ($CDCl_3$) δ 7.1–8.4 (m, 9)

prepared via methylenephosphorane extrusion are given in Table I.

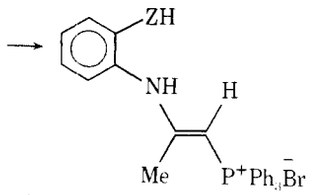
The phenylethynyl salt **12**, prepared according to the method of Viehe and Franchimont,[12] was used in the synthesis of several other substituted phosphonium salts (**15**) that were cyclized to the corresponding phenyl-substituted heterocycles **16** (Table I).

The following reactions were undertaken in the hope of determining the relative reactivity of salt **11** vs. **12** in the overall reaction (Scheme I).

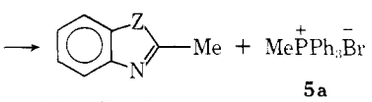
Aniline was allowed to react with the salts **11** and **12** under



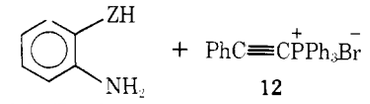
10A, Z = S
B, Z = O
C, Z = NH
D, Z = CH_2
E, Z = CONH



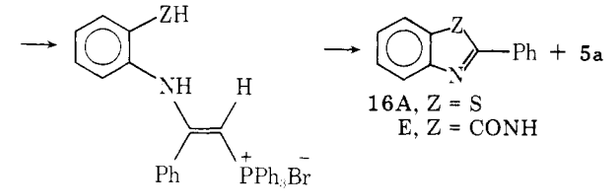
13A, Z = S
B, Z = O
C, Z = NH
D, Z = CH_2
E, Z = CONH



14A, Z = S
B, Z = O
C, Z = NH
D, Z = CH_2
E, Z = CONH

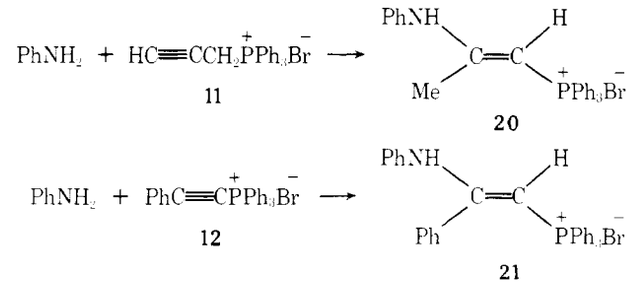


10A, Z = S
E, Z = CONH



15A, Z = S
E, Z = CONH

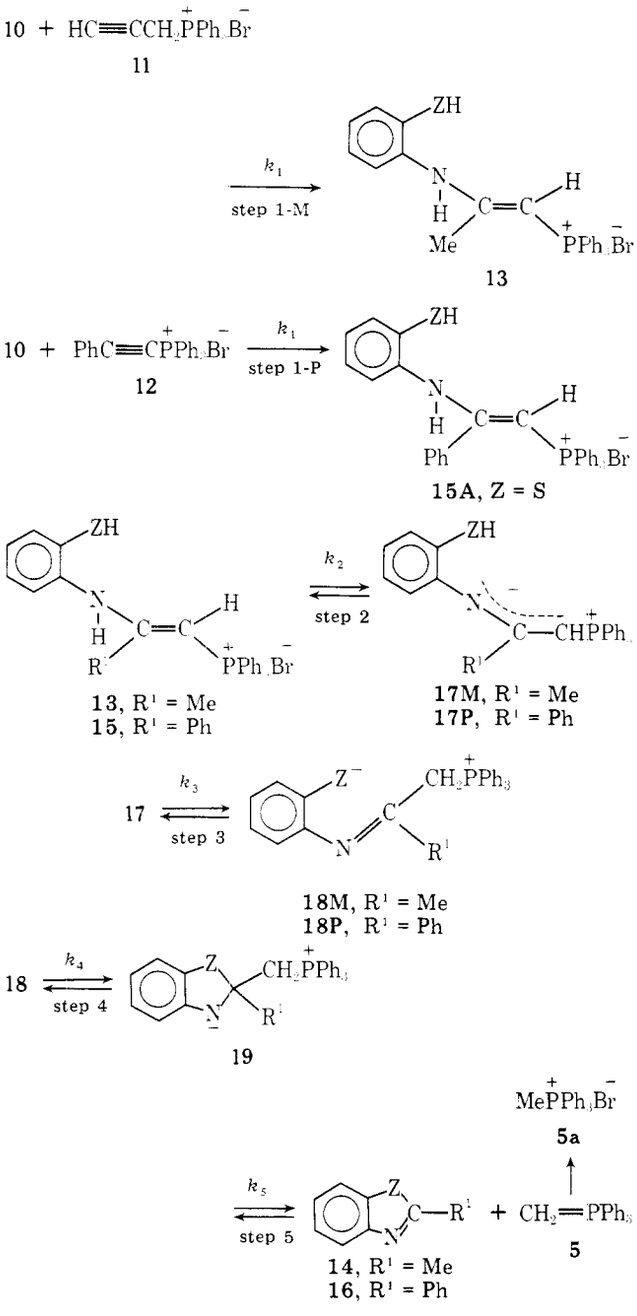
identical conditions. The addition of aniline was monitored by NMR spectroscopy. There was a quantitative conversion of aniline and **11** into **20** after only 15 min. Under the same conditions, aniline and **12** showed essentially no reaction after



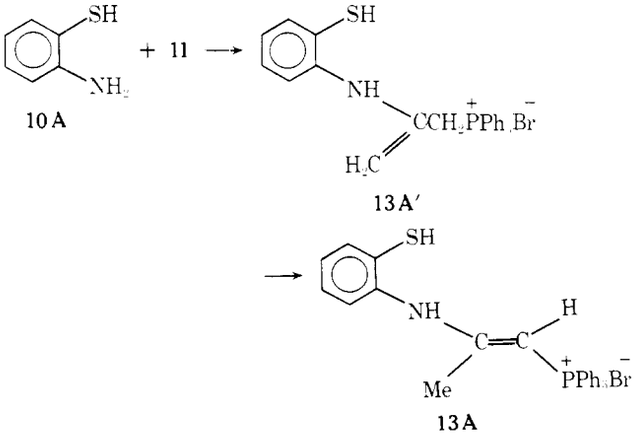
5 h. Therefore, the relative rate k_1 for **11** can be assumed to be greater than k_1 for **12** (rate step 1-M > rate step 1-P; see Scheme I).

The propargyl salt **11** and 2-aminothiophenol (**10A**) were allowed to react in acetonitrile at room temperature in the hope of obtaining the adduct **13A**. The conjugate addition product **13A'** was obtained. We have previously shown[11] (on

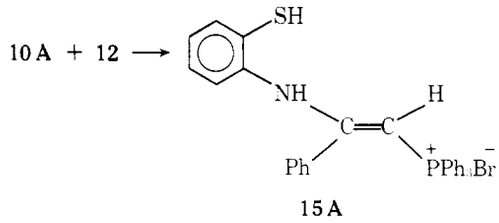
Scheme I



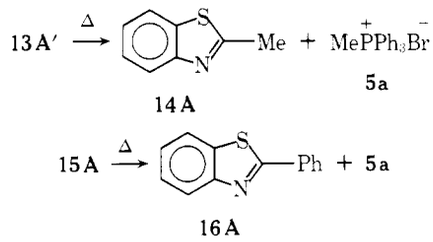
reacting methanol and 11) that allyl-substituted salts, such as **13A'**, would lie on the pathway from 11 and **10A** to **13A.**



The reaction of **10A** and 12 under similar conditions gave adduct **15A.**



Thermolysis of **13A'** and **15A** under identical conditions showed that the rate of formation of **14A** from **13A'** is greater than the rate of formation of **16A** from **15A,** as determined by observing the rate of formation of methyltriphenylphosphonium bromide (**5a**) by NMR spectroscopy (see Table IV and Experimental Section).

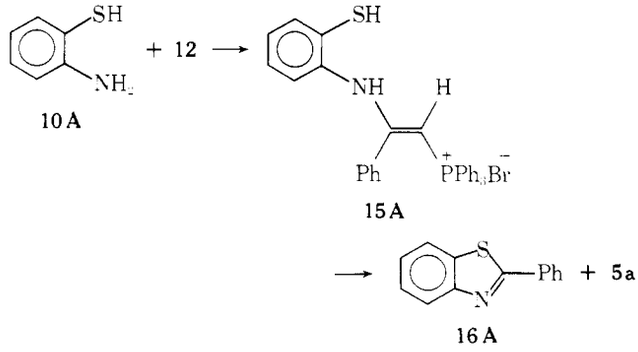


Since both **20** and **14A** were formed from 11 and **13A',** respectively, faster than **21** and **16A** were formed from 12 and **15A,** one can conclude that the overall rate of reaction of 11 to form heterocycles is faster than the rate of reaction from 12.

The effect of the heteroatom (Z) on the formation of species 14 was investigated by examining the conditions necessary for reaction to occur, and the percent yield was obtained. Treatment of *o*-mercaptoaniline (Z = S) (**10A**) with 11 in refluxing acetonitrile overnight gave **14A** directly, presumably via the intermediacy of **13A,** in 62% yield without the necessity of any additional base (see Table I). The intermediates **13B, 13C,** and **13D** could be isolated from the reaction of the appropriate **10** and 11 under similar conditions. Thus, where ZH is SH in **10** the ring closure reaction (**13** → **14**) is more rapid than where ZH is OH, NH_2, or CH_3. By examining the crude reaction mixtures of **13B, 13C,** and **13D** (see Table II), run under identical base-catalyzed (NaH) conditions, it was found that the relative reactivities of **13** parallel the relative acidity of the ZH moiety (SH > OH > NH_2 >>> CH_3). No methylene extrusion reaction is observed for adduct **13D** (ZH = CH_3).

Compound **15A** was prepared from 12 and *o*-aminothiophenol (**10A**) in 79% yield in the same manner as **14A** was prepared by the addition of **10A** to 11.

On heating **15A** under reflux in acetonitrile for 5 days, **16A** and **5a** were obtained. On heating **15A** for 1 h with a catalytic amount of base, a 53% yield of **16A** was obtained. Confirmation of structure was based on ^1H NMR spectroscopy, exact mass determination, and melting point[14] (see Table I).



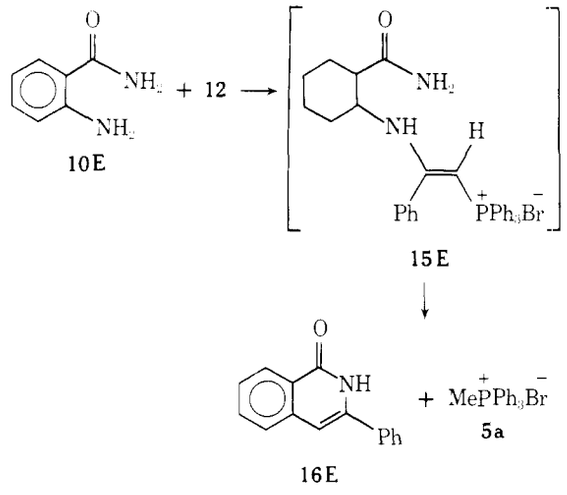
On treating anthranilamide (**10E**) with 12 in the manner which yielded **15A** from **10A** and 12, no reaction was observed.

Table II. Preparation of Heterocycles 14[a]

Salt	Registry no.	Hetero-atom	% unreacting starting material	% product 14
13B	66255-65-0	O	0	100
13C	66290-51-5	N	48	55
13D	66255-44-5	C	100	0

[a] % composition of crude reaction mixture after 3 days in refluxing MeCN.

However, when the reaction time was increased to 5 days, 2-phenylquinazolin-4-one (**16E**) was isolated in 45% yield, presumably via the intermediate phosphonium salt **15E**. Methyltriphenylphosphonium bromide (**5a**) was also found to be present in the reaction mixture. Physical data compared favorably with that reported in the literature.[13]



A consideration of the possible rate-determining step of the reaction of **13** or **15** would lead us to suggest that it should be the conjugate addition step, step 4 in Scheme I, because of the following reasons. (a) One would expect the proton-transfer reactions, steps 2 and 3 in Scheme I, to be relatively rapid.[15] (b) The relative rate of formation of **16** (R^1 = Ph; Scheme I) from the corresponding **19** would also be expected to be greater than that for the formation of **14** (R^1 = Me) since both the inductive effect of the phenyl ring and the formation of the double bond in conjugation with the phenyl ring should enhance the formation of **16** over **14.** (c) However, we have just shown that **13A** (for **A'**) yields the product at a greater rate than **15A.** Therefore, our conclusion is that step 4 (Scheme I) is the rate-determining step and that k_4 for **18M** (Z = S) is greater than k_4 for **18P** (Z = S).

In summary, we have shown this methylene extrusion reaction to be a useful synthetic tool for the preparation of a variety of heterocyclic species (Table I). We have also shown that the rate of formation of the heterocycle from (2-phenylethynyl)triphenylphosphonium bromide (**12**) is slower than the rate from triphenyl(prop-2-ynyl)phosphonium bromide (**11**).

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer, mass spectra on a CEC (duPont) 21-110B mass spectrometer at an ionization potential of 70 eV, and ^{1}H NMR spectra on a Perkin-Elmer Model R12B spectrometer using tetramethylsilane (Me_4Si) as an internal standard. All melting points are uncorrected and were obtained on a Thomas-Hoover capillary melting point apparatus. Elemental analyses were performed by Micro Analysis Inc., Wilmington, Del., and MHW Laboratories, Garden City, Mich. Yields obtained by integration of the appropriate signals in the ^{1}H NMR spectrum of the product(s) vs. the signal of a predetermined amount of an added standard are regarded as being accurate to ca. ±10%. Any analytical and spectral data not included in the text may be found in the tables.

All reactions were run under dry nitrogen using anhydrous solvents. All solutions were concentrated to an oil with a rotary evaporator. All glassware was oven-dried for at least 2 h at a temperature of 120 °C. Sodium hydride (57% in mineral oil) was washed three times with hexane prior to use in any reaction.

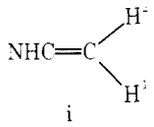
(2-Phenylethynyl)triphenylphosphonium Bromide (12). (2-Phenylethynyl)triphenylphosphonium bromide (**12**) was prepared according to the method of Viehe and Franchimont.[12]

[2-(*N*-Phenyl)amino-2-phenylethenyl]triphenylphosphonium Bromide (21). The method of Hoffmann and Foerster[20] was used to prepare [2-(*N*-phenyl)amino-2-phenylethenyl]triphenylphosphonium bromide (**21**).

[2-(*N*-Phenyl)aminoprop-1-enyl]triphenylphosphonium Bromide (20). The method of W. P. Murray[21] was used to prepare [2-(*N*-phenyl)aminoprop-1-enyl]triphenylphosphonium bromide (**20**).

Triphenyl(prop-2-ynyl)phosphonium Bromide (11).[22] To a solution of triphenylphosphine (210 g, 0.80 mol) and 1,4-dioxane (400 mL) in a 1-L Morton flask fitted with a reflux condenser, mechanical stirrer, and a dropping funnel was added 90 mL of 48% HBr over a 30-min period. After the reaction became homogeneous, 96 g (0.80 mol) of propargyl bromide was added over a 90-min period. The reaction mixture was stirred for 3 h and filtered. Recrystallization with 2-propanol gave 230 g (75%) of **11** as white crystals: mp 179 °C dec (lit.[22] mp 156–158 °C); ^{1}H NMR (CF_3COOH) δ 2.3 (m, 1, J_{HH} = 2.8 Hz, J_{PH} = 6.5 Hz, C≡CH), 4.5 (dd, 2, J_{HH} = 2.8 Hz, J_{PH} = 15.0 Hz, $-CH_2P$); IR 1440, 1110 (P–C) cm^{-1}.

Preparation of [2-(*N*-*o*-(Mercaptophenyl)aminoprop-2-enyl]triphenylphosphonium Bromide (13A'). Into a flask were placed equimolar amounts (0.01 mol) of 2-aminothiophenol and **11** with 100 mL of acetonitrile. The mixture was stirred at room temperature for 1 week. The mixture was filtered. The filtrate was added slowly to ethyl acetate with stirring. The resulting crystals were recovered by filtration, yielding 3.15 g (61%) of **13A'** as a yellow solid: mp 145–150 °C; ^{1}H NMR ($CDCl_3$) δ 4.35 (s, 1, SH), 4.80 (bd, 1, H^1; see structure i), 4.90 (d, 2, J_{PH} = 13 Hz, $-CH_2P$), 5.35 (bd, 1, H^2; see i), 6.4–8.1 (m, 20, –NH, aromatic); IR 1430, 1115 (P–C) cm^{-1}.



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[2-(*N*-*o*-(Mercaptophenyl)amino-2-phenylethenyl]triphenylphosphonium Bromide (15A). The salt **15A** was prepared in the same manner as **13A'** above except that **12** was substituted for **11.** Recrystallization with methylene chloride/ethyl acetate gave 4.45 g (79%) of **15A** as yellow crystals: mp 175–176 °C; ^{1}H NMR ($CDCl_3$) δ 5.65 (d, 1, =CH, J_{PH} = 15.3 Hz), 6.25–7.90 (m, 26, –SH, –NH, aromatic).

General Procedure for the Preparation of Heterocycles (14). Equimolar amounts of the phosphonium salt **13** and sodium hydride were allowed to react in a 250-mL flask. The salt was dissolved in 100 mL of acetonitrile, and then sodium hydride was added. The mixture was stirred under reflux until TLC indicated completion. After cooling, the mixture was filtered. The filtrate was concentrated to an oil and dissolved in a minimal amount of methylene chloride, and ethyl acetate was added to initiate crystallization of **5a.** After filtration, the filtrate was again concentrated to an oil (crude product **14**). The workup is described below. The physical data are recorded in Table I.

2-Methylbenzimidazole (14C). The oil obtained from treating compound **13C** by the general procedure was recrystallized in water to yield **14C** as white crystals.

2-Methylbenzoxazole (14B). The oil obtained from treating compound **13B** by the general procedure was distilled to yield the desired product **14B** as a colorless liquid.

2,5-Dimethylbenzoxazole (14G). The oil obtained by treating compound **13G** by the general procedure was distilled to yield the desired product **14G** as a yellow liquid.

Treatment of [2-(*N*-*o*-Methylphenyl)aminoprop-1-enyl]triphenylphosphonium Bromide (13D) with Sodium Hydride. The initial oil obtained by treating compound **13D** by the general procedure was crystallized from methylene chloride/ethyl acetate to yield **13D** as white crystals (82% recovery). NMR spectroscopy of the crude reaction mixture indicated 100% starting material (**13D**) present and 0% of **5a** present.

Table III. Preparation of Phosphonium Salts 20 and 21[a]

	20	21	
h/min	% product 20	% unreacted aniline	% product 21
0:00	0	100	0
0:05	45		
0:10	78		
0:15	100	100	0
2:00		92	0
5:00		90	0
24:00		77	0

[a] % composition of reaction mixture.

2-Methylbenzothiazole (14A). A 5.0-g amount of *o*-mercaptoaniline was dissolved in acetonitrile in a 250-mL flask. An equimolar amount of the salt **13A** (15.2 g, 0.04 mol) was added, and the mixture was stirred and refluxed for 1 day. The mixture was cooled, concentrated to an oil, dissolved in a minimum amount of methylene chloride, and then slowly added to ethyl acetate with stirring. The mixture was filtered. The residual crystals were recrystallized from methylene chloride/ethyl acetate to yield 9.7 g of **5a,** mp 230–231 °C. The filtrate was concentrated to an oil and distilled to give **14A** as a colorless liquid.

2-Phenylquinazolin-4-one (16E). Equimolar amounts (0.01 mol) of *o*-aminobenzamide and **12** were allowed to react in a 250-mL flask by dissolving the amine in acetonitrile and then adding **12.** The mixture was stirred under reflux for 5 days. After cooling, the solid was collected by filtration and recrystallized in ethanol/water to yield **16E** as white crystals. An exact mass determination by mass spectrometry gave a mass of 222.0794 (calcd, 222.0793).

2-Phenylbenzothiazole (16A). Into a 250-mL flask was placed 4.4 g (0.01 mol) of **12** and 5 g (large excess) of *o*-aminothiophenol. A catalytic amount of sodium hydride was then added. The mixture was stirred at reflux for 1 h. After cooling, the mixture was filtered. The filtrate was concentrated to an oil and dissolved in a minimal amount of methylene chloride, and ethyl acetate was added to initiate crystallization of **5a.** After filtration, the filtrate was concentrated to a solid. The solid was recrystallized in ethanol (absolute) to yield **16A** as white crystals. An exact mass determination by mass spectrometry gave a mass of 211.0450 (calcd, 211.0456).

Rate of Formation [2-(*N*-Phenyl)aminoprop-1-enyl]triphenylphosphonium Bromide (20) from Aniline and 11. Equimolar amounts (0.02 mol) of aniline and **11** were allowed to react in a 250-mL flask by dissolving the amine in exactly 200 mL of chloroform and then adding the phosphonium salt. The mixture was stirred at room temperature. The disappearance of aniline was followed using NMR spectroscopy by taking 5-mL aliquots, concentrating to an oil, and redissolving in deuteriochloroform. Trichloroethylene was added as an internal reference. The appearance of a doublet at δ 4.75 (J_{PH} = 15.0 Hz) and a singlet at δ 2.05 indicated the formation of **20.** The results are summarized in Table III.

Rate of Formation of [2-(*N*-Phenyl)amino-2-phenylethenyl]triphenylphosphonium Bromide (21) from Aniline and 12. Equimolar amounts (0.01 mol) of aniline and **12** were allowed to react in a 250-mL flask by dissolving the amine in exactly 100 mL of chloroform and then adding the phosphonium salt. The mixture was stirred at room temperature. The disappearance of aniline was followed using NMR spectroscopy by taking 2-mL aliquots, concentrating to an oil, and redissolving in deuteriochloroform. Trichloroethylene was added as an internal reference. The appearance of a doublet at δ 5.56 (J_{PH} = 13.3 Hz) and a singlet at δ 5.2 indicated the formation of **21.** The results are summarized in Table III.

Thermolysis of [2-(*N*-*o*-Mercaptophenyl)amino-2-phenylethenyl]triphenylphosphonium Bromide (15A). In an NMR tube **15A** (0.187 mmol) was dissolved in deuteriochloroform. Cyclohexane was added as an internal reference. The sealed NMR tube was heated in an oil bath at 80 ± 2 °C. The disappearance of **15A** was followed by NMR spectroscopy. The appearance of a doublet at δ 3.3 (J_{PH} = 13.3 Hz) indicated the formation of methyltriphenylphosphonium bromide (**5a**). The results are summarized in Table IV.

Table IV. Thermolysis of 13A and 15A at 80 °C

	13A′		15A
h/min	% unreacted 13A′	% product 5a	% product 5a
0:00	100	0	0
0:05	92	0	0
0:15	82	7	
0:35			<1
0:45	57	19	
0:50			7
1:00	43	30	
1:15	38	34	16
1:45	15	41	15
2:15	6	53	13
2:45	0	67	16
3:45	0	68	31
7:00			46
15:00			58
17:00			57

Thermolysis of [2-(*N*-*o*-Mercaptophenyl)aminoprop-2-enyl]triphenylphosphonium Bromide (13A′). In an NMR tube **13A′** (0.2 mmol) was dissolved in deuteriochloroform. Cyclohexane was added as an internal reference. The sealed NMR tube was heated in an oil bath at 80 ± 2 °C. The disappearance of **13A′** was followed by NMR spectroscopy. The appearance of a doublet at δ 3.3 (J_{PH} = 13.3 Hz), indicating the formation of methyltriphenylphosphonium bromide (**5a**), and a singlet at δ 2.85, indicating 2-methylbenzothiazole (**14A**), was observed. The results are summarized in Table IV.

Preparation of Heterocycles 14B, 14C, and 14D: Percent Composition Comparison. Equimolar amounts (2.5 mmol) of the phosphonium salt **13B, 13C,** or **13D** and sodium hydride were allowed to react in a 50-mL flask by dissolving the salt in 10 mL of acetonitrile at room temperature. After 25 min, sodium hydride and an additional 20 mL of acetonitrile were added. The mixture was stirred at reflux for 3 days. After cooling, the mixture was filtered and concentrated to an oil. The percent composition was determined by NMR spectroscopy with methylene chloride as an internal reference. The results are summarized in Table II.

Registry No.—**5a,** 1779-49-3; **11,** 2091-46-5; **12,** 34387-64-9; **13A,** 66255-45-6; **13A′,** 66290-52-6; **13G,** 66290-53-7; **15A,** 66255-46-7; **20,** 66255-47-8; **21,** 66255-48-9; aniline, 62-53-3; triphenylphosphine, 603-35-0; 1,4-dioxane, 123-91-1; 2-aminothiophenol, 137-07-5; *o*-aminobenzamide, 88-68-6.

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