Reactions of Phosphorus Compounds. 39. Synthesis and Reactions of [2-(Aziridin-1-yl)alkenyl]triphenylphosphonium Bromides

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Aziridines (**1**) were allowed to react with (2-propynyl)triphenylphosphonium bromide (**2**) to yield (2-aziridinylallyl)-triphenylphosphonium bromide (**3**) at low temperature and (2-aziridinyl-1-propenyl)triphenylphosphonium bromide (**4**) directly, or on heating from **3**. (Phenylethynyl)triphenylphosphonium bromide (**5a**) yields (2-phenyl-2-aziridinylvinyl)triphenylphosphonium bromide (**6**). The salts from aziridine and **2** or **5a** yield (2-methyl- (**14a**) and (2-phenyl-2-pyrrolin-3-yl)triphenylphosphonium bromide (**14b**), respectively, on heating in acetonitrile. Treatment of several of the salts, **4a** and **4b**, with aniline at 70 °C yields the alkylated anilines **13a** and **13b**, respectively. 2-Vinylaziridines (**15**) and **2** yield substituted [(2*H*-1,3,4,7-tetrahydroazepin-2-ylidene)methyl]triphenylphosphonium bromides (**16**), while **15** and **5a** or (1-propyn-1-yl)triphenylphosphonium bromide (**5b**) give (1*H*-2,5-dihydroazepin-6-yl)triphenylphosphonium bromides (**17**) via hetero-Cope rearrangements. Compounds **14a** and **17a** are N-alkylated, whereas **16b** is alkylated α to the triphenylphosphonium moiety. Compounds **14a** and **16a** undergo the Wittig reaction with aldehydes in the normal manner. Proton and ^{13}C NMR spectra are reported for most of the compounds.

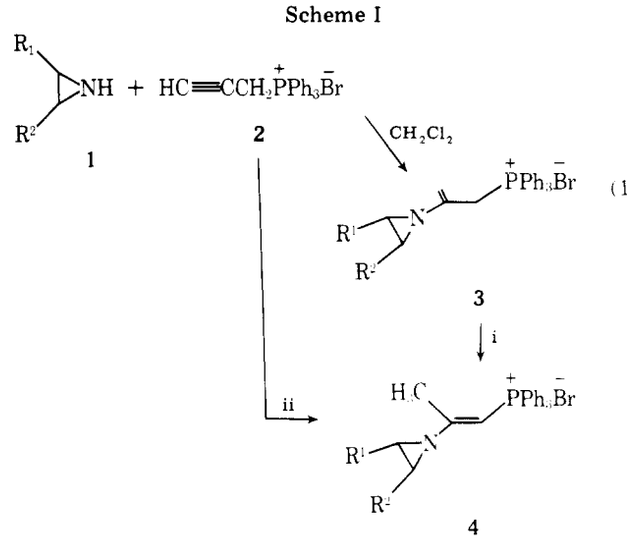
Recent reviews have reflected current interest in the synthesis and chemistry of heterocycles bearing phosphorus-containing substituents.[2,3] Preceding work in this laboratory has dealt with the synthesis of such heterocycles from unsaturated organophosphonium salts.[4a-e] These syntheses have employed both cycloaddition and intramolecular Wittig reaction routes to form the heterocycle. This paper describes our current efforts to prepare phosphorus-substituted heterocycles via the rearrangements of the activated aziridine synthon.

Results and Discussion

When aziridines **1** were allowed to react with (2-propynyl)-triphenylphosphonium bromide (**2**) in methylene chloride (eq 1) at the temperature given in Table I, the corresponding adducts **3** were usually produced (Scheme I, Table I). From the low temperature addition of **1c** to **2**, however, only the "conjugated" adduct **4c** was isolated. The "conjugated" adducts **4a** and **4b** were also prepared either via heating the isolated intermediate **3** in chloroform or acetonitrile [eq 1 (i)] or directly by heating **1** and **2** in methylene chloride [eq 1 (ii)] (without isolation of intermediate **3**). Similarly, the *N*-vinylaziridine **6** was obtained from the reaction of **1a** and (phenylethynyl)triphenylphosphonium bromide (**5a**) (eq 2, Scheme I).

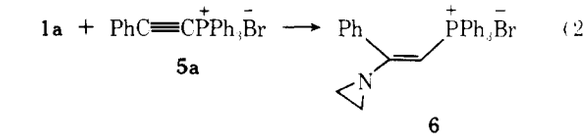
These products were characterized by their field desorption (FDMS) and chemical ionization mass spectra (CIMS), IR, ^1H NMR, and ^{13}C NMR spectra. The IR spectra of compounds **3** showed a weak absorption at ~1630 cm^{-1} corresponding to the terminal double bond, while compounds **4** and **6** showed a strong absorption at ~1560 cm^{-1}, in good agreement with the behavior of double bonds of other β-aminovinylphosphonium salts.[4f,g] The NMR spectra of **3** (with the exception of **3d**) could not be obtained at normal probe temperatures (~30–40 °C). Attempts to do so provided only a spectrum of **4**. However, ^1H and ^{13}C NMR spectra of **3a** were obtained at −10 °C. The ^{13}C NMR spectra are given in Table II for compounds **3a**, **4a**,[4i] and **4b**. The ring protons of adducts

Scheme I



(1)

a, $R^1 = R^2 = H$; b, $R^1 = R^2 = (CH_2)_4$; c, R^1 = Ph, R^2 = H; d, R^1 = PhCO, $R^2 = p\text{-}O_2NC_6H_4$



(2)

Table I. [2-(Aziridin-1-yl)-2-propenyl]triphenylphosphonium Bromides (3) and [2-(Aziridin-1-yl)-1-propenyl]triphenylphosphonium Bromides (4)

		Equation 1			Equation 1 (i)				Equation 1 (ii)	
	R^1, R^2	3, mp (°C)	% yield	T, °C time, h	4, mp (°C)	% yield	Solvent	T, °C/ time, h	% yield	T, °C/ time, h
a	H, H	132–136	85	0–10/0.5	122–127	84	$CHCl_3$	$40/8 \times 10^{-4}$	81	0[a] → 40/0.5
b	$(CH_2)_4$	110–117	71	0–10/0.5	97–117		CH_3CN	81/16	84	0[a] → 25/0.5
c	Ph, H				153–160				92	0[a] → 5/0.5
d	PhC(O), $p\text{-}O_2NC_6H_4$	124–136	53	25/1.33						

[a] Reactants were mixed at 0 °C over a period of 0.5 h, and then the mixture was warmed briefly to the second temperature for the time given.

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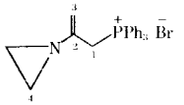
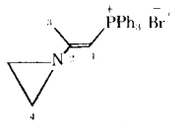
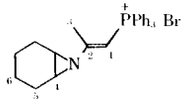
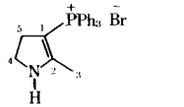
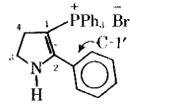
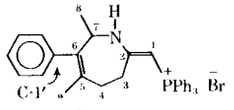
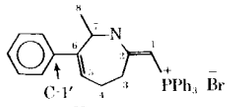
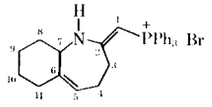
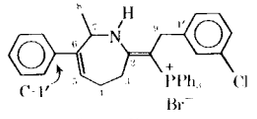
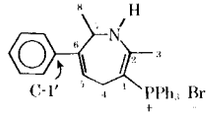
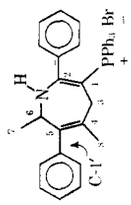
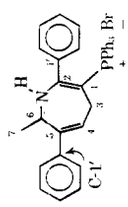
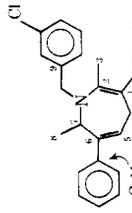
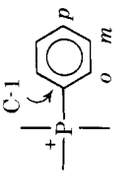
Table II. ^{13}C Chemical Shifts[a] and ^{13}C–^{31}P Coupling Constants[b] of β-Vinylphosphonium Salts

No.	Compd	1	2	3	4	5	6	7	8	9	10	11	C-1	*o*	*m*	*p*	C-1′	Other
3a		31.9 (48.2)	146.4 (11.0)	103.3 (10.4)	28.2								118.2 (87.3)	134.0 (9.8)	130.0 (12.8)	134.7 *		
4a		80.7 (106)	175.8 (10.4)	22.2 (3.7)	28.6								120.3 (91.6)	133.2 (9.8)	130.5 (12.2)	134.7 *		
4b		78.9 (105)	176.7 (9.8)	21.7 *	39.6	23.7	19.7						120.5 (91.6)	133.2 (9.8)	130.5 (12.2)	134.6 *		
14a		64.9 (125.7)	169.7 (22.0)	15.6 *	46.1 (11.0)	31.5 (9.8)							121.9 (91.6)	133.4 (11.0)	130.1 (13.4)	134.2 *		
14b		66.9 (124.5)	170.1 (19.5)	46.3 (9.8)	32.1 (9.8)								120.5 (91.5)	135.5 (9.8)	129.7 (12.2)	134.0 *	134.7 *	*o′, m′, p′****
16a		56.4 (114)	171 (~14–15)	30.8 (5)	31.6	**	137.8	53.4	22.9	21.3			124.6 (84)	133.0 (10.4)	129.8 (12.2)	133.6 *	142.3	*o′, m′, p′****
16b		57.6 (123.3)	171 (12.2)	31.2 *	25.7	**	143.2	52.5	22.3				124.0 (91.6)	132.8 (9.8)	129.8 (12.2)	133.7 *	142.4	*o′, m′, p′****
16c		56.9 (123.3)	172.1 (13.4)	33.2 (4.7)	35.6 (36.9)	121	140	57.5	24.9	27.2	24.9	36.9 (35.6)	124.5 (91.6)	133.0 (11.0)	129.8 (12.2)	133.7 *		
19		69.4 (111.1)	167.2 (19.5)	33.6 *	25.7	**	143.4	53.1	22.4	45.8 (47.6)			122.9 (89.1)	**	**	**	142.1	1′, 138.6 (11.0); *o′, m′, p′*; 2′, 3′, 4′**
17a		62.6 (109.9)	162.0 (19.5)	21.1 *	26.4 (7.3)		143.8	51.7	22.4				123.0 (89.1)	**	**	**	140.7	*o′, m′, p′****

17b		69.7 (108.6)	164.3 (22.0)	36.0 (9.7)		138.4	50.9	21.7	19.4		121.4 (89.1)	**	129.7 (12.2)	**	140.1	1′, 137 (~2–3); *o′, m′, p′*; 2′, 3′, 4′**
17c		69.2 (109.9)	165.0 (20.8)	29.4 (7.9)		145.0	51.9	21.5			121.8 (89.1)	**	**	**	140.1	1′, 137 (~2–3); *o′, m′, p′*; 2′, 3′, 4′**
20		61.8 (107.4)	161.5 (21)	26.5 *	27.3 (~4)		141.3	47.9	12.2	64.2	122.4 (89.1)	**	**	**	137.7	*o′, m′, p′*; 2′, 3′, 4′**

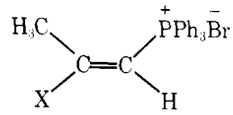
[a] The chemical shifts are in ppm referenced to internal Me_4Si. The numbering system for the β-aminopropenyl moiety is shown on the structure. The numbering system for the PPh_3 moiety is as follows:



All samples were run in $CDCl_3$. A double asterisk indicates that the peaks were obscured by the aromatic region. [b] The coupling constants are in parentheses and are in Hz. The digital resolution was ±0.6 Hz; an asterisk indicates that the coupling was less than resolution capable. [c] Reference 4i.

4 exhibited NMR signals with chemical shifts approximately 1 ppm downfield from those of **1**. The chemical shifts of the vinyl protons of these adducts likewise appear considerably downfield from those found for other β-(alkylamino)vinylphosphonium salts.[4f–i] In a similar manner, the chemical shift of the vinyl carbon next to phosphorus in **4** was deshielded relative to the same resonance in other β-(alkylamino)vinylphosphonium salts.[4h] This phenomenon (i.e., the relative deshielding of the vinyl protons and carbons adjacent to phosphorus in β-aziridinylvinylphosphonium salts) has been discussed in a recent publication.[4i]

While IR, ^1H NMR, and ^{13}C NMR spectra were of considerable utility in the characterization of these phosphonium salts, electron-impact mass spectra provided extremely little information, presumably due to the salts' low volatility. Field desorption mass spectroscopy (FD), which has previously been found useful for the molecular weight determination of phosphonium halides,[5] was therefore tried with a number of these salts. Although compounds **7**, **8**, and **10** gave essentially



7, X = $CH_2CH_2CH_2N$–

8, X = $CH_2CH_2CH_2CH_2CH_2N$–

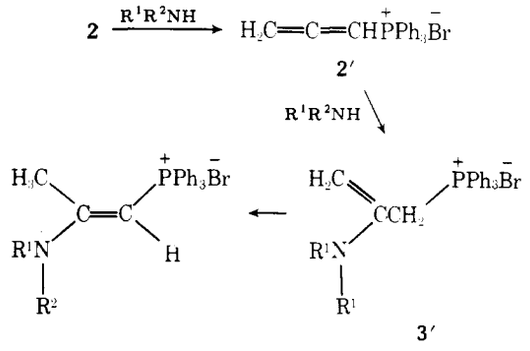
9, X = $(CH_3)_2N$–

10, X = CH_3NH–

one-line spectra providing the correct molecular weight of the corresponding cation, FD spectra of **4a**, **4b**, and **6** were quite complex and could not be used for molecular weight determination. Interestingly, the FD mass spectrum of **3d** showed two main line groups corresponding to the cation (M^+) and a cation/anion cluster (M^+Br^- − 1). Another more general method was sought, however, since the field desorption method was unsuccessful with **4a**, **4b**, and **6**. McLafferty and co-workers[6] have reported a chemical ionization technique wherein relatively involatile compounds react in the solid phase directly with the ionized gas. Munson et al.[7] have recently applied this technique to the analysis of the phosphonium halides reported in this work. From this method correct M^+ lines were obtained for not only **7**, **8**, and **9**, but also for **3**, **4**, and **6**. Thus, the latter technique seems to have wider applicability than FDMS to the analysis of these phosphonium salts. Both methods have been used in the analysis of various other compounds in this paper.

Isolation of compound **3** is consistent with the following mechanism of addition of amines to **2** (Scheme II). The intermediacy of **2′** has been conclusively shown in the conjugate additions of nucleophiles to **2**.[4f] Compounds corresponding to **3** or **3′** from the addition of alcohols to **2** have also been

Scheme II



3′

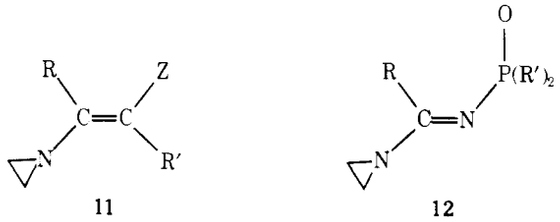
Table III. 2*H*-1,5,6,7-Tetrahydroazepines (16) and 2*H*-1,5-Dihydroazepines (17)

Compd	R	R^1	R^2	R^3	% yield	Mp, °C	Conditions (T, °C/time, h)
16a		CH_3	Ph	CH_3	95	232–234	0[a] → 20/0.5
16b		CH_3	Ph	H	90	229–234	0[a] → 20.0.5
16c		$(CH_2)_4$		H	74	90–115	0[a] → 20/0.5
17a	CH_3	CH_3	Ph	H	90	242–246	81/6
17b	Ph	CH_3	Ph	CH_3	71	214–222	81/20
17c	Ph	CH_3	Ph	H	73	130–150	81/20

[a] Reactants were mixed at 0 °C over a period of 0.5 h, and then the mixture was warmed briefly to 20 °C for the time given.

isolated,[4f] and a phosphonate analogue of **3a** has been prepared.[8]

Compounds **4** and **6** are uniquely "activated" aziridines. Many examples of compounds with the general structure **11** (where Z is an electron-withdrawing group) are known.[9-13] Examples containing the phosphorus moiety, iminophosphonates and phosphoramides **12**, have also been synthe-

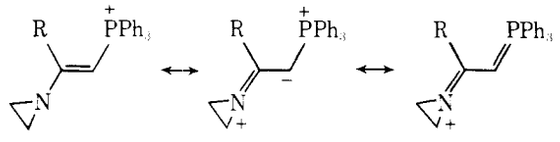


11 **12**

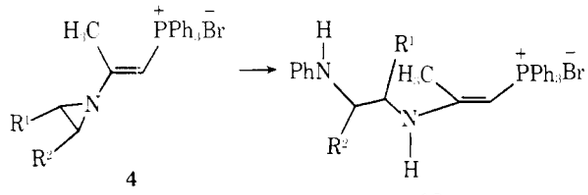
R = Ar, NHAr; R′ = –OPh, –N⟨

sized.[14] However, **4** and **6** are the only examples of **11**, to our knowledge, where Z is a phosphonium group.

Although the resonance forms depicted below for **4** are apparently not as important as those for **7–10**,[4i] consideration of this diminished resonance might nevertheless lead one to predict that **4** and **6** have quite electrophilic ring carbons.



Some alkylation reactions typical of "activated" aziridines were therefore attempted. Thus, when aziridines **4a** and **4b** were treated with aniline at 70 °C, compounds **13** were obtained in 95% yield (eq 3).

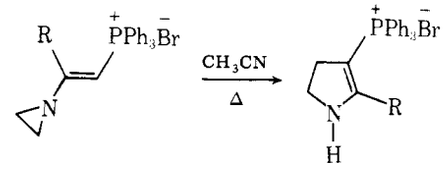


4 **13** (3)

a, $R^1 = R^2 = H$; b, $R^1 = R^2 = (CH_2)_4$

Nucleophile-Catalyzed Rearrangements. Nucleophile-catalyzed rearrangements of *N*-vinylaziridines to pyrrolines[9-11] are rather sparse compared to those of acyl-activated aziridines.[15,16] Indeed, rearrangements of *N*-vinylaziridines in this manner are known to be quite difficult,[17] often producing only ring-opened products.[9-17] In this laboratory, attempts at these rearrangements with 2-(aziridin-1-yl)-vinylphosphonium salts were only partially successful.

In refluxing acetonitrile, compounds **4a** and **6** rearrange to the 2-pyrrolines **14a** and **b** in 65 and 86% yields, respectively (eq 4). The spectral and analytical data support the assigned structures. The ^{13}C NMR spectra of **14** are given in Table II. Compound **4b** under similar conditions was recovered unchanged.



4a, R = CH_3
6, R = Ph

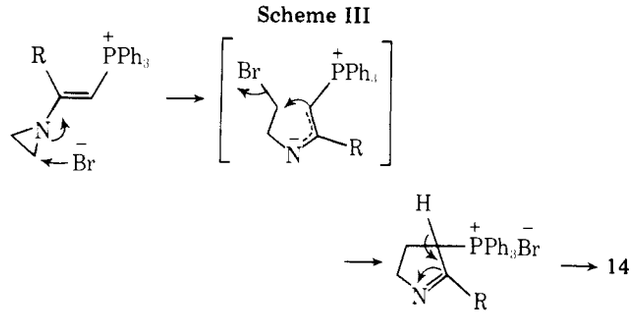
14a, R = CH_3
b, R = Ph

(4)

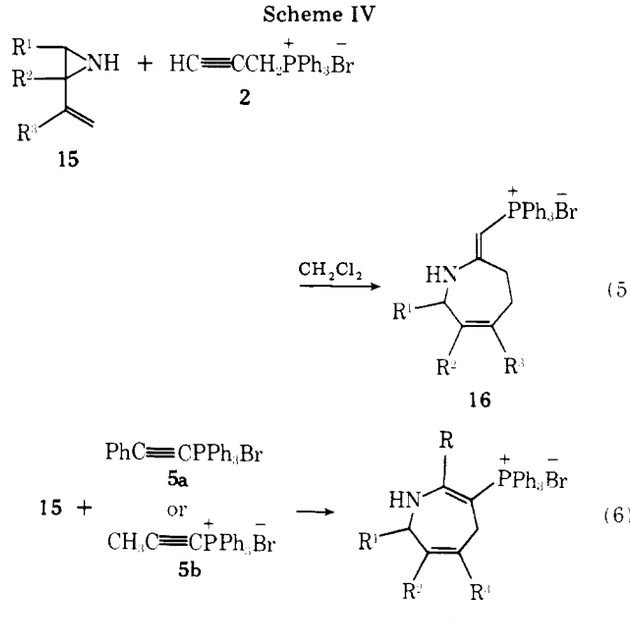
A suggested mechanism for the formation of **14** is depicted in Scheme III. Although analogous phosphonates have been synthesized,[18a] previous attempts to prepare a pyrroline ring containing a triphenylphosphonium substituent have been unsuccessful.[18b,c]

Hetero-Cope Rearrangements. From the reaction of 2-vinylaziridines **15** with **2** in methylene chloride, no compounds corresponding to **3** or **4** were isolated. Instead, the tetrahydroazepine derivatives **16** were obtained (eq 5, Scheme IV, Table III). In a similar manner, treatment of **5a** of (1-propynyl)triphenylphosphonium bromide (**5b**) with **15** in

Scheme III



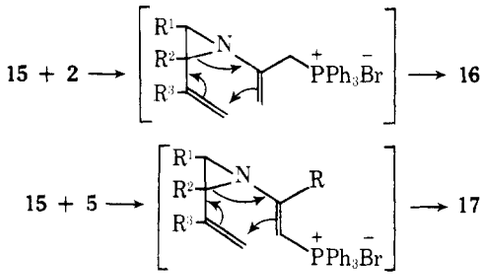
Scheme IV



15 **16** (5)

17 (6)

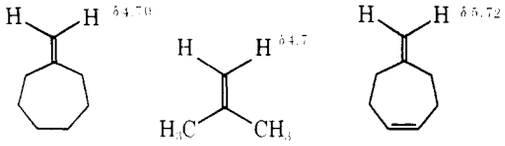
Scheme V



acetonitrile produced the dihydroazepine derivatives **17** (eq 6, Scheme IV, Table III).

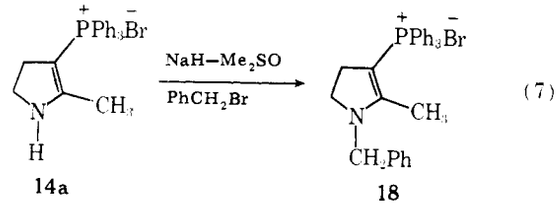
The unique ability to form the dihydroazepine ring where the triphenylphosphonium moiety β to the amino group is placed on the ring 2 position (**17**) or on an exocyclic methylene position at the ring 1 position (**16**) is due to the nature of the intermediate unsaturated phosphonium salt formed prior to the hetero-Cope rearrangement. The reaction of **15** and **2** undoubtedly proceeds by a mechanism similar to that in Scheme II, but the intermediate corresponding to **3′** undergoes a hetero-Cope rearrangement[22] to give **16** (Scheme V) instead of becoming conjugated. The addition of **15** to **5** occurs in the same manner as the addition of aziridines to other activated alkynes,[12a,13] followed by the hetero-Cope rearrangement. The facility of these processes should make them appealing as a ready synthesis of the azepine ring system; such syntheses are scarce in the literature.[22b]

The ^{1}H NMR spectra of compounds **16** exhibit a resonance for the vinyl proton next to phosphorus considerably deshielded (δ 5.30–5.47) from the corresponding shifts of compounds **7–10** (δ 3.68–4.05).[4i] The carbon next to phosphorus in these compounds, on the other hand, gives a ^{13}C chemical shift in good agreement with those of **7–10**.[4i] The reasons for the anomalous ^{1}H shifts are not clear; however, a similar chemical shift difference may be noted in the ^{1}H NMR spectra of methylidenecycloheptane[19] or 2-methylpropene[20] vs. 5-methylidenecycloheptene[21] (below).

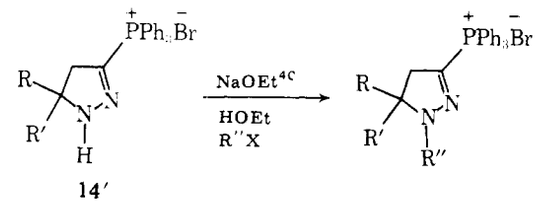


The ^{13}C NMR spectra of **16** and **17** are given in Table II. Additional evidence for the structure of **16a** was provided by an off-resonance decoupling experiment carried out with its ^{1}H NMR spectrum. Irradiation of the broad 1-H multiplet at δ ~4.6 changed the exchangeable proton at δ 9.80 (NH) from a broad doublet to a singlet and the doublet at δ 1.38 (overlapping with the singlet at δ 1.27) to a singlet.

Alkylation of 14, 16, and 17. The alkylation of salt **14a** by benzyl bromide in sodium hydride–dimethyl sulfoxide (eq 7)

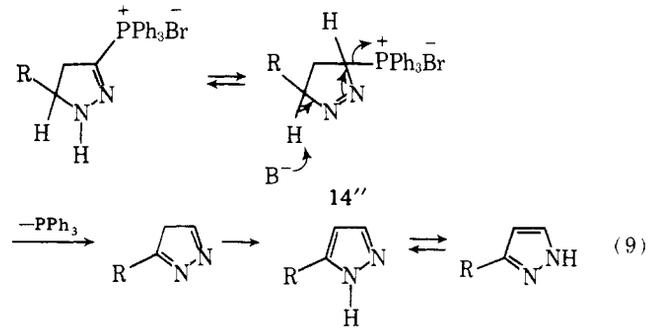


(7)



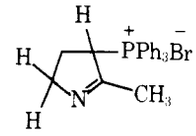
(8)

occurred, as predicted by previous work (eq 8),[4c] to give N-alkylated product **18**. Thus, both the 2-pyrrolinyl- and 2-pyrazolinylphosphonium ylides alkylate on nitrogen. When R or R′ is a hydrogen, however, **14′** eliminates triphenylphosphine to produce pyrazoles (eq 9); no alkylation products



(9)

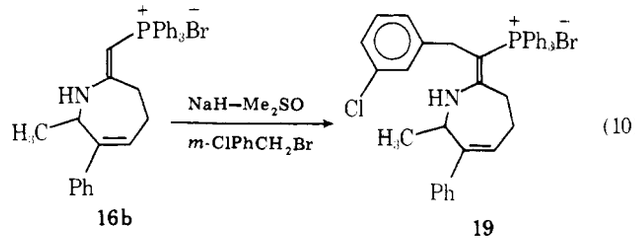
were reported.[4c] Compound **14a**, on the other hand, is apparently more stable to basic conditions. A reasonable rationale for this difference may be found in the mechanism suggested by eq 9. The polarization of the C=N bond in **14‴**



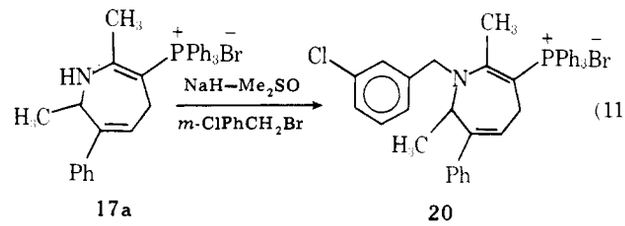
14‴

counterbalances the electronegativity of the phosphonium moiety, thus reducing the acidity of the protons on the 5 position, whereas this effect is not present in **14″** and the vinylogous β elimination is relatively easy to accomplish.

Reaction of compound **16b** with *m*-chlorobenzyl bromide in sodium hydride–dimethyl sulfoxide produced compound **19** (eq 10), while reaction of its isomer, compound **17a**, under the same conditions produced compound **20** (eq 11). The former reaction has provided the first instance in this labo-



(10)



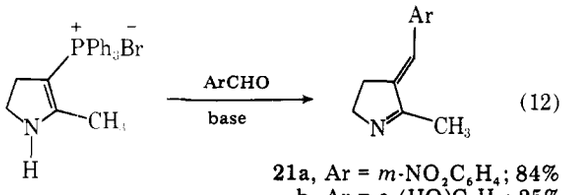
(11)

ratory of C alkylation of a β-aminovinylphosphonium salt. It seems likely that the decreased steric hindrance of the carbon next to phosphorus in **16** vs. the same carbon in **14a**, **14′**, or **17** might account for this difference in reactivity.

The ^{13}C NMR spectra of **19** and **20** are reported in Table II. Since no ^{13}C spectra of β-aminovinylphosphonium salts with an α substituent have previously been reported, support for the assigned structures of **19** and **20** was sought by comparison of their ^{13}C NMR spectra with spectra of similar compounds in this work. The ^{13}C spectra of five other such compounds are also presented in Table II. A preliminary inspection of this table shows that the ^{13}C–^{31}P coupling constant for C-2 of the α-substituted compounds is larger than the same coupling constant for compounds without an α substituent

by 4.5–12.2 Hz. Thus, the $J(^{13}C-^{31}P)$ of 19.5 Hz for **19** vs. 12.2 Hz for its precursor **16b** supports the assigned structure for **19**. Also, from Table II one may note that the chemical shifts for C-1 without a substituent range from 54.1 to 59.3 ppm, whereas with a substituent on C-1 they range from 61.8 to 69.7 ppm. Thus, the ^{13}C chemical shift of C-1 in these compounds is displaced an average of 10 ppm to lower field by adding an α substituent. Hence, the value of 69.4 ppm for C-1 in **19** provides additional support for the assigned structure.

Wittig Reactions of 14 and 16. Lastly, the use of these phosphonium salts as Wittig reagents was investigated. Treatment of an ethanolic solution of **14a** and *m*-nitrobenzaldehyde with sodium ethoxide in ethanol produced the pyrroline derivative **21a** (eq 12). Although a similar procedure



(12)

14a

21a, Ar = *m*-$NO_2C_6H_4$; 84%
b, Ar = *o*-$(HO)C_6H_4$; 25%

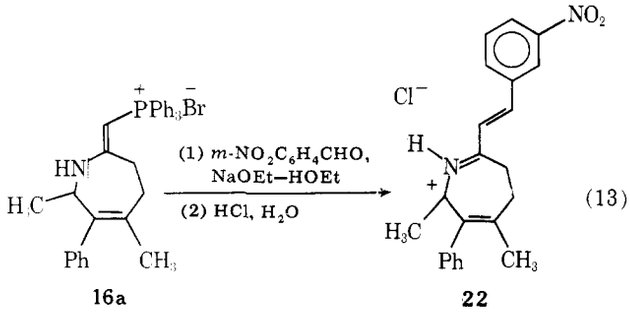
Ar = *m*-$NO_2C_6H_4$, base = NaOEt–HOEt;
Ar = *o*-$(HO)C_6H_4$, base = NaH–Me_2SO

was unsuccessful for the reaction of **14a** and salicylaldehyde, the desired pyrroline, **21b**, was obtained by the use of sodium hydride–dimethyl sulfoxide (eq 12).

The structures of **21** were supported by their ^1H NMR spectra, EI mass spectra, and analytical data. Additionally, an off-resonance decoupling ^1H NMR experiment was performed with **21a**. The ^1H NMR spectrum of this compound exhibits both allylic coupling between the benzylidene proton and the 4 position hydrogens ($J \sim 3$ Hz) and homoallylic coupling between the methyl group and the 5 position hydrogens ($J \sim 1.5$ Hz). Irradiation of the complex multiplet at $\delta \sim 4.3$ (5 position CH_2) changes the resonance at δ 2.33 (CH_3) from a triplet to a singlet and converts the triplet of doublets at δ 3.02 (4 position CH_2) to a doublet. Irradiation of the resonance at δ 3.02 changes the triplet at δ 7.05 (vinyl H) to a singlet, and, finally, irradiation of the δ 2.33 resonance changes the $\delta \sim 4.3$ multiplet to a triplet ($J \simeq 5.7$ Hz).

Again, for reasons similar to those illustrated in eq 9, the resulting pyrrolines, **21**, are stable to the basic reaction conditions, whereas the analogous pyrazolines undergo a base-catalyzed rearrangement to pyrazoles.[4c]

In a similar reaction, treatment of an ethanolic solution of azepine **16a** and *m*-nitrobenzaldehyde with sodium ethoxide in ethanol produced compound **22** (eq 13), isolated as a hydrochloride salt.



(13)

16a **22**

We have demonstrated in this paper that heterocycles bearing phosphorus-containing substituents, namely compounds **14**, **16**, and **17**, may be prepared via the synthesis and rearrangement of [2-(aziridin-1-yl)alkenyl]triphenylphosphonium bromides. These heterocycles may be alkylated or used in a Wittig olefin synthesis.

Experimental Section

Carbon-13 spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{13}C data were taken at an operating frequency of 22.63 MHz. The ^{13}C chemical shifts are reported as referenced to Me_4Si. All samples were run in approximately 0.05 M solutions of $CDCl_3$ at 32 °C with broad band ^1H decoupling (except compounds **3a**, **4a**, and **4b**, which were run at approximately −10, −5, and 0 °C, respectively). The proton spectra were obtained on either a Perkin-Elmer R-12 or a Varian A-60A spectrometer and were referenced to Me_4Si. Concentrations used for the proton spectra were similar to those used for the ^{13}C spectra. The ^1H spectra of compound **3a** was taken at −10 °C; all others were taken at normal probe temperatures (~30–40 °C). Infrared spectra were recorded on either a Perkin-Elmer 337 or a Unicam SP1100 spectrometer. FD, CI, and EI mass spectra were all obtained on a duPont CEC 21-110B modified for the respective methods. Melting points were taken with a Mel-Temp apparatus and are uncorrected. Elemental analyses were obtained from Micro Analysis, Inc., Wilmington, Del., Chemalytics, Inc., Tempe, Ariz., and Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Aziridines **1b** and **c** were prepared by the method of Hassner et al.[23] and purified by distillation. Aziridines **15** were prepared by the method of Chaabouni et al.[24] and purified by column chromatography (silica gel; petroleum ether (30–60 °C)/ether = 4.1). Aziridines **1a** and **d** were graciously donated to this laboratory by Dr. Harold W. Heine. The (2-propynyl)triphenylphosphonium bromide (**2**),[4f] (1-propynyl)triphenylphosphonium bromide (**5b**),[4f] and (phenylethynyl)triphenylphosphonium bromide (**5a**)[25] were prepared as previously described. All other reagents and solvents were obtained from either Aldrich Chemical. Co., Eastman Organic Chemical Co., or Fisher Scientific Co. *m*-Nitrobenzaldehyde (Eastman) was recrystallized from ethanol, and aniline (Fisher) was distilled before use. Acetonitrile, dimethyl sulfoxide, and chloroform were purified as described in the literature.[26]

[2-(Aziridin-1-yl)-2-propenyl]triphenylphosphonium Bromides (3; eq 1), [2-(Aziridin-1-yl)-1-propenyl]triphenylphosphonium Bromides [4; eq 1 (ii)], and [2-(Aziridin-1-yl)-2-phenylethenyl]triphenylphosphonium Bromide (6). The following general procedure was used for the preparation of **3**, **4**, and **6**. While stirring a slurry of **2** or **5a** in methylene chloride (20 mL/g of **2** or **5a**) at the temperature given in Table I, the appropriate aziridine **1** (1.01 mol/mol of **2** or **5a**) in methylene chloride (20 mL/g of **1**) was added over the time given in Table I. In the preparation of **3** or **6**, the mixture was stirred for an additional 5 min and then poured into anhydrous ethyl ether (70 mL/g of **2** or **5a**). For the preparation of **4**, the mixture was warmed briefly to the temperature given in Table I [eq 1 (ii)] and then poured into anhydrous ethyl ether. After stirring vigorously for several minutes, the precipitate was filtered and dried in a vacuum oven (2–3 mm, 40 °C). In addition to the ^{13}C NMR data for **3a**, **4a**, and **4b** given in Table II and melting point and yield data in Table I, the following data were collected.

[2-(Aziridin-1-yl)-2-propenyl]triphenylphosphonium Bromide (3a): IR (KBr) 3050, 2990, 2870, 2840 (CH), 1630 (C=C), 1580 (phenyl), 1110 (CP), 750, 720, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$ at −10 °C) δ 1.4–2.1 (m, 4, CH_2CH_2), 4.3–5.0 (m, 4, CH_3P and H_2C=), 7.4–8.2 (m, 15, C_6H_5); CIMS (isopentane) *m/e* (relative intensity) 344 (45.76, M^+).

Anal. Calcd for $C_{23}H_{23}BrNP$ (424.309): C, 65.10; H, 5.46. Found: C, 64.96; H, 5.44.

[2-(7-Azabicyclo[4.1.0]hept-7-yl)-2-propenyl]triphenylphosphonium Bromide (3b): IR (KBr) 3050, 2980, 2930, 2850 (CH), 1620 (C=C), 1110 (CP), 750, 710, 690 (phenyl) cm^{-1}; CIMS (isopentane) *m/e* (relative intensity) 398 (100, M^+).

[2-(2-Benzoyl-3-(*p*-nitrophenyl)aziridin-1-yl)-2-propenyl]triphenylphosphonium Bromide (3d): IR (KBr) 1670 (C=O), 1620 (C=C), 1520, 1350 (NO_2), 1110 (CP), 750, 720, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (d, 1, CH, $J_{HH} \simeq 2$ Hz), 3.5C (d, 1, CH, $J_{HH} \simeq 2$ Hz), ~4.5 (brd d, 2, CH_2P, $J_{PH} \simeq 20$ Hz), 4.92 (d, 1, =CH, $J_{HH} \simeq 7$ Hz), 5.12 (d, 1, =CH, $J_{HH} \simeq 7$ Hz), 6.8–8.0 (m, 24, aromatic H's); FDMS *m/e* (relative intensity) 569 (79, M^+), 647 (9.4, M^+ $^{79}Br^-$ − 1), 649 (17, M^+ $^{81}Br^-$ − 1); CIMS (isopentane) *m/e* 569 (6.14, M^+), 279 [100, $(Ph_3PO + 1)^+$].

[2-(Aziridin-1-yl)-1-propenyl]triphenylphosphonium Bromide (4a): IR (KBr) 3050, 3000 (CH), 1580 (phenyl), 1560 (C=C), 1110 (CP), 765, 750, 730, 720, 695 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87 (s, 3, CH_3), 2.55 (s, 4, CH_2CH_2), 5.31 (d, 1, =C(H)P, $J_{PH} \simeq 16$ Hz), 7.4–8.0 (m, 15, C_6H_5); CIMS (isopentane) *m/e* (relative intensity) 344 (4.19, M^+).

[2-(7-Azabicyclo[4.1.0]hept-7-yl)-1-propenyl]triphenylphos-

phonium Bromide 4b: IR (KBr) 1550 (C=C), 1110 (CP), 750, 720, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–1.5 (m, 4, $-CH_2CH_2-$), 1.80 (s, 3, CH_3), 1.7–2.1 (m, 4, $-CH_2CCCH_2-$), 3.00 (m, 2, $-CHCH-$), 5.18 (d, 1, =C(H)P, $J_{PH} \simeq 16$ Hz), 7.5–8.0 (m, 15, C_6H_5); CIMS (isopentane) *m/e* (relative intensity) 398 (40.56, M^+).

[2-(2-Phenylaziridin-1-yl)-1-propenyl]triphenylphosphonium Bromide 4c: IR (KBr) 3050, 2900, 2870 (CH), 1570 (C=C), 1108 (CP), 860, 750, 740, 710, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (d, 3, CH_3, $J_{PH} \simeq 1.2$ Hz), 2.58 (d, 1, H trans to H, $J_{trans} \simeq 4$ Hz), 3.32 (d, 1, H cis to H, $J_{cis} \simeq 7$ Hz), 4.08 (dd, 1, C(H)Ph, $J_1 \simeq 7$ Hz, $J_2 \simeq 4$ Hz), 5.41 (d, 1, =C(H)P, $J_{PH} \simeq 16.8$ Hz), 7.1–7.5 (m, 5, Ph on ring), 7.5–8.1 (m, 15, PPh_3); CIMS (isopentane) *m/e* (relative intensity) 420 (28.29, M^+).

Anal. Calcd for $C_{29}H_{27}BrNP$ (500.409): C, 69.60; H, 5.44. Found: C, 69.35; H, 5.57.

[2-(Aziridin-1-yl)-2-phenylethenyl]triphenylphosphonium Bromide (6): 85%; mp 118–124 °C; IR (KBr) 3050, 3040, 2970 (CH), 1580 (phenyl), 1550 (C=C), 1110 (CP), 765, 753, 740, 730, 720, 705, 685 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (s, 4, CH_2CH_2), 6.13 (d, 1, =C(H)P, $J_{PH} \simeq 14$ Hz), 7.20 (s, 5, PhC=), 7.5–8.2 (m, 15, PPh_3); CIMS (isopentane) *m/e* (relative intensity) 406 (26.01, M^+).

4a and 4b via Equation 1 (i). The corresponding phosphonium salt (**3a** or **3b**) was dissolved in the appropriate solvent (0.236 mmol/mL) and then heated to the temperature and for the time prescribed in Table I. The solution was then added to anhydrous ethyl ether (500 mL/g of phosphonium salt) with vigorous stirring. Filtration and vacuum drying (2–3 mm, 40 °C) provided materials whose spectral data agreed favorably with **4a** and **4b** as prepared above. Due to the highly hygroscopic nature of **4b** produced by this process, an accurate determination of the percent yield could not be made.

[2-(Alkylamino)-1-propenyl]triphenylphosphonium Bromides (7–10). Compounds **7** and **8** were prepared by a procedure similar to that employed in the preparation of **3a**, with the exception that the addition was carried out at room temperature or slightly below. Yields and infrared data are as follows (NMR data are reported elsewhere).[4i]

[2-(Azetidin-1-yl)-1-propenyl]triphenylphosphonium Bromide (7): yield 95%; mp 232–238 °C (from CH_2Cl_2–EtOAc); IR (Nujol mull) 1540 (C=C), 1100 (CP), 750, 720, 685 (phenyl) cm^{-1}; FDMS *m/e* (relative intensity) 358 (100, M^+); CIMS (isopentane) m/e 358 (100, M^+).

[2-(Piperidin-1-yl)-1-propenyl]triphenylphosphonium Bromide (8): yield 94%; mp 233–239 °C (from CH_2Cl_2–EtOAc); IR (Nujol mull) 1540 (C=C), 1100 (CP), 750, 745, 715, 690 (phenyl) cm^{-1}; FDMS *m/e* (relative intensity) 386 (100, M^+); CIMS (isopentane) 386 (92.13, M^+).

Compounds **9** and **10** were prepared by the following general procedure. An aqueous solution of greater than 2 M excess of the amine hydrochloride was made strongly basic with sodium hydroxide. This solution was extracted several times with methylene chloride, and the extracts were dried over anhydrous $MgSO_4$ and then added to a slurry of **2** in methylene chloride in the same manner as for the preparation of **7** and **8**. Addition to anhydrous ethyl ether, filtration, and vacuum drying provided the following yields (NMR data are reported elsewhere).[4i]

[2-(*N,N*-Dimethylamino)-1-propenyl]triphenylphosphonium Bromide (9): yield 82%; mp 208–214 °C (from CH_2Cl_2–EtOAc); IR (Nujol mull) 1560 (C=C), 1100 (CP), 760, 745, 715, 690 (phenyl) cm^{-1}; CIMS (isopentane) *m/e* (relative intensity) 346 (100, M^+).

Anal. Calcd for $C_{23}H_{25}BrNP$ (426.329): C, 64.79; H, 5.91. Found: C, 64.89; H, 5.75.

[2-(*N*-Methylamino)-1-propenyl]triphenylphosphonium Bromide (10): yield 95.6%; mp 270–276 °C (from CH_2Cl_2–EtOAc); IR (Nujol mull) 1560 (C=C), 1110 (CP), 750, 720, 690 (phenyl) cm^{-1}; FDMS *m/e* (relative intensity) 332 (100, M^+).

Alkylation of Aniline with 3 or 4. A mixture of 3a, 4a, or 3b and aniline (molar ratio ~1:25) was stirred magnetically and heated to 70 °C for 15 h. Addition of the resulting red solution to anhydrous ethyl ether (250 mL/mmol of phosphonium salt) with vigorous stirring produced the following respective products.

[2-(2-Anilinoethylamino)-1-propenyl]triphenylphosphonium Bromide (13a): yield 96%; mp 204–214 °C (CH_2Cl_2–heptane); IR (Nujol mull) 3200 (NH), 1600 (phenyl), 1530 (C=C), 1500 (phenyl), 1100 (CP), 760, 750, 740, 715, 685 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87 (s, 3, CH_3), 3.1–3.8 (m, 4, CH_2CH_2), 3.84 (d, 1, =C(H)P, $J_{PH} \simeq 14$ Hz), 5.75 (brd s, 1, NHPh, exchanges quickly with D_2O), 6.4–7.3 (m, 5, PhN), 7.3–7.9 (m, 15, PPh_3), 8.64 (brd s, 1, NHC=, exchanges slowly with D_2O).

Anal. Calcd for $C_{29}H_{30}BrN_2P$ (517.441): C, 67.31; H, 5.84. Found: C, 67.50; H, 5.54.

[2-(2-Anilinocyclohexylamino)-1-propenyl]triphenylphosphonium Bromide (13b): yield 95%; mp 254–261 °C (CH_2Cl_2–EtOAc); IR (Nujol mull) 3200 (NH), 1590 (phenyl), 1540 (C=C), 1100 (CP), 755, 740, 715, 685 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.3 (m, 8, cyclohexyl ring), 1.68 (s, 3, CH_3), 3.3–3.9 (m, 2, CHCH), 4.09 (d, 1, =C(H)P, $J_{PH} \simeq 15$ Hz), 6.5–7.2 (m, 5, PhN), 7.2–7.9 (m, 15, PPh_3), 8.4 (brd s, 1, NHC=); FDMS *m/e* (relative intensity) 491 (100, M^+).

Anal. Calcd for $C_{33}H_{36}BrN_2P$ (571.53): C, 69.35; H, 6.35. Found: C, 69.86; H, 6.55.

(2-Methyl-2-pyrrolin-3-yl)triphenylphosphonium Bromide (14a). A round-bottom flask fitted with a reflux condenser was charged with 3.00 g (7.08 mmol) of **3a** or **4a**, approximately 0.4 mL of pyridine, and 100 mL of acetonitrile. The mixture was refluxed for 24 h, after which time 300 mL of anhydrous ethyl ether was added. The resulting suspension was stirred vigorously (magnetic) for 15 min and then filtered. The filtrate was poured into 1500 mL of anhydrous ethyl ether. After stirring for 15 min, the mixture was filtered; the filter cake and gummy yellow residue left in the flask were dissolved in 100 mL of methylene chloride. Slow addition of this solution to 1500 mL of anhydrous ethyl ether (with vigorous stirring) produced 1.95 g (65%) of a yellow-white powder which was immediately placed in a vacuum oven (40 °C, 2–3 mm): mp 80–110 °C; IR (KBr) 3150 (H-bonded NH), 2850 (CH), 1550 (C=C), 1110 (CP), 760, 720, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (brd s, 3, CH_3), 2.67 (brd t, 2, CH_2 at 4 position, $J_{HH} \simeq 10$ Hz), 3.85 (brd t, 2, CH_2 at 5 position, $J_{HH} \simeq 10$ Hz), 7.5–8.1 (m, 15, C_6H_5), 8.53 (brd s, 1, NH, D_2O exchangeable); FDMS *m/e* (relative intensity) 344 (100, M^+); CIMS (isopentane) *m/e* 344 (100, M^+).

(2-Phenyl-2-pyrrolin-3-yl)triphenylphosphonium Bromide (14b). In a round-bottom flask fitted with a reflux condenser was placed 1.00 g (2.06 mmol) of **6**, 5 drops of pyridine, and 50 mL of acetonitrile. The mixture was refluxed for approximately 15 h and then cooled and added slowly to 900 mL of anhydrous ethyl ether. The white precipitate which was filtered off, after vacuum oven drying, weighed 0.89 g (89%), mp 212–217 °C dec. After five recrystallizations from methylene chloride–ethyl acetate, the product melted at 234–236 °C: IR (KBr) 3150 (H-bonded NH), 2930, 2850 (CH), 1580 (phenyl), 1550 (C=C), 1110 (CP), 770, 750, 720, 695 (p,enyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.85 (brd t, 2, CH_2 at 4 position, $J_{HH} \simeq 11$ Hz), 4.10 (brd t, 2, CH_2 at 5 position, $J_{HH} \simeq 11$ Hz), 6.8–7.5 (m, 5, Ph), 7.5–8.4 (m, 16, PPh_3 and NH); FDMS *m/e* (relative intensity) 406 (100, M^+).

Anal. Calcd for $C_{28}H_{25}BrNP$ (486.390): C, 69.14; H, 5.18. Found: C, 68.99; H, 5.76.

Preparation of 16. To a slurry of **2** in methylene chloride (12.5 mL/g of **2**), kept at 0 °C, was added the appropriate 2-vinylaziridine **15** (1.01 mol/mol of **2**) in methylene chloride (12.5 mL/g of **2**) over the period of time specified in Table III. The mixture was allowed to warm to room temperature and was then poured into anhydrous ethyl ether (250 mL/g of **2**) with vigorous stirring. Filtration and vacuum drying (2–3 mm, 40 °C) provided the crude products listed below, which were recrystallized from methylene chloride–ethyl acetate. ^{13}C NMR data are listed in Table II; percent yield and melting point data are listed in Table III.

[(5,7-Dimethyl-6-phenyl-2*H*-1,3,4,7-tetrahydroazepin-2-ylidene)methyl]triphenylphosphonium Bromide (16a): IR (KBr) 3170 (NH), 3070, 3050, 3020, 2960, 2890 (CH), 1580 (C=CH), 1101 (CP), 763, 750, 713, 700, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s, 3, $=CCH_3$), 1.38 (d, 3, CH_3, $J_{HH} \simeq 7.2$ Hz), 1.6–2.0 (m, 2, CH_2), 2.3–2.7 (m, 2, CH_2) 4.3–4.9 (brd m, 1, HCN), 5.44 (d, 1, =C(H)P, $J_{PH} \simeq 16.8$ Hz), 7.0–8.1 (m, 20, C_6H_5), 9.80 (brd d, 1, NH, $J_{HH} \simeq 7.2$ Hz); CIMS (isopentane) *m/e* (relative intensity) 474 (100, M^+).

Anal. Calcd for $C_{33}H_{33}BrNP$ (554.515): C, 71.48; H, 6.00. Found: C, 71.65; H, 5.93.

[(6-Phenyl-7-methyl-2*H*-1,3,4,7-tetrahydroazepin-2-ylidene)methyl]triphenylphosphonium Bromide (16b): IR (KBr) 3230, 3140 (NH), 1640 (C=C), 1600 (C=CN), 1110 (CP), 785, 765, 750, 734, 721, 715, 695, 690 (phenyl) cm^{-1}; H NMR ($CDCl_3$) δ 1.44 (d, 3, CH_3, $J_{HH} \simeq 7$ Hz), 1.6–2.9 (m, 4, CH_2CH_2), 4.6–5.0 (m, 1, CHN), 5.30 (d, 1, =C(H)P, $J_{PH} \simeq 16.2$ Hz), 5.49 (t, 1, =C(H)C, $J_{HH} \simeq 5$ Hz), 7.25 (s, 5, C_6H_5), 7.4–8.1 (m, 15, $P(C_6H_5)_3$), 9.70 (brd d, 1, NH, $J_{HH} \simeq 6$ Hz); FDMS *m/e* (relative intensity) 460 (100, M^+).

Anal. Calcd for $C_{32}H_{31}BrNP$ (540.489): C, 71.11; H, 5.78. Found: C, 71.29; H, 6.04.

[(1*H*-2,3,4,6,7,8,9,9a-Octahydro-1-benzazepin-2-ylidene)-methyl]triphenylphosphonium Bromide (16c): IR (KBr) 3220 (NH), 1595 (NC=C), 1105 (CP), 750, 715, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–3.0 (m, 12, alkyl H's), 3.85–4.35 (m, 1, CHN), ~5.3 (m under =C(H)P, 1, =C(H)C), 5.47 (d, 1, =C(H)P, $J_{PH} \simeq 17$ Hz), 7.5–8.2 (m, 15, C_6H_5), ~9 (brd d 1, NH); FDMS *m/e* (relative inten-

sity) 424 (100, M^+).

Preparation of 17. A mixture of **5**, the appropriate vinylaziridine **15** (1.05 mol/mol of **5**), and acetonitrile (15 mL/g of **5**) was refluxed for the time specified in Table III. After cooling, the mixture was added to anhydrous ethyl ether (250 mL/g of **5**) with stirring. Filtration and vacuum drying (2–3 mm, 40 °C) provided the crude products listed below, which were recrystallized from methylene chloride–ethyl acetate. ^{13}C NMR data are listed in Table II; percent yield and melting point data are listed in Table III.

(2,7-Dimethyl-3-phenyl-1*H*-2,5-dihydroazepin-6-yl)triphenylphosphonium Bromide (17a): IR (KBr) 3220 (NH), 1615 (C=C), 1555 (NC=C), 1101 (CP), 765, 756, 750, 715, 690 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (d, 3, CH_3, $J_{HH} \simeq 7.2$ Hz), 1.81 (s, 3, $=CCH_3$), 2.2–3.2 (m, 2, CH_2), 4.8–5.2 (m, 1, CHN), 5.85 (t, 1, =C(H)C, $J_{HH} \simeq 8.4$ Hz), 7.1–8.0 (m, 20, C_6H_5), 8.86 (dd, 1, NH, $J_1 \simeq 6$ Hz, $J_2 \simeq 5$ Hz); FDMS *m/e* (relative intensity) 460 (100, M^+).

Anal. Calcd for $C_{32}H_{31}BrNP \cdot H_2O$ (558.497): C, 68.82; H, 5.96. Found: C, 69.44; H, 5.98.

(2,4-Dimethyl-3,7-diphenyl-1*H*-2,5-dihydroazepin-6-yl)triphenylphosphonium Bromide (17b): IR (KBr) 3350, 3230 (NH), 3060, 2990, 2840 (CH), 1630 (C=C), 1540, 1510 (NC=C), 1101 (CP), 767, 759, 710, 695 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (d, 3, CH_3, $J_{HH} \simeq 5.4$ Hz), 1.58 (s, 3, CH_3), 2.0–2.9 (m, 2, CH_2), 5.4–5.8 (m, 1, CHN), 6.9–8.5 (m, 26, C_6H_5's and NH).

Anal. Calcd for $C_{38}H_{35}BrNP$ (615.579): C, 74.02; H, 5.72. Found: C, 74.14; H, 5.60.

(2-Methyl-3,7-diphenyl-1*H*-2,5-dihydroazepin-6-yl)triphenylphosphonium Bromide (17c): IR (KBr) 3200 (NH), 3060, 3000, 2940, 2890 (CH), 1630 (C=C), 1525 (NC=C), 1105 (CP), 760, 720, 710, 695 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (d, 3, CH_3, $J_{HH} \simeq 6.6$ Hz), 3.15 (dd, 2, CH_2, $J_{PH} \simeq 12$ Hz, $J_{HH} \simeq 7.8$ Hz), 5.1–5.6 (m, 1, CHN), 6.02 (t, 1, =C(H)C, $J_{HH} \simeq 7.8$ Hz), 6.5–8.2 (m, 26, C_6H_5's and NH); FDMS *m/e* (relative intensity) 522 (100, M^+).

Alkylation of 14, 16, and 17. To a solution of **14**, **16**, or **17** in dimethyl sulfoxide (~0.3 M) under dry nitrogen was added an equimolar amount of sodium hydride (as a 57% mineral oil dispersion). The mixture was stirred for 1 h before adding the appropriate alkylating agent (~3 mol/mol of phosphonium salt). After stirring overnight, the mixture was added to anhydrous ethyl ether (75 mL/mL of Me_2SO) with stirring. A gummy precipitate formed, from which the ethereal supernatant was decanted. The residue was triturated with a few milliliters of methylene chloride and filtered into anhydrous ethyl ether (~50 mL/mL of CH_2Cl_2) with vigorous stirring. Filtration provided the crude product.

Purification of **18** was effected in the following manner. The crude product was dissolved in methylene chloride (~10 mL/g of phosphonium salt) and then added with stirring to ethyl acetate (~500 mL/g). The mixture was filtered, and the filtrate was poured into anhydrous ethyl ether (~1500 mL/g) with stirring. The purified product was filtered.

Purification of **19** or **20** was effected in the following manner. The crude product was dissolved in excess methylene chloride (*n* mL) and added to ethyl acetate (*n* mL). The methylene chloride was removed by boiling until a slight cloudiness appeared. The mixture was allowed to cool, and the supernatant liquid was poured into anhydrous ethyl ether (2*n* mL). Purification provided purified phosphonium salt. ^{13}C NMR data of **19** and **20** are reported in Table II. Other data are as follows.

(1-Benzyl-2-methyl-2-pyrrolin-3-yl)triphenylphosphonium Bromide (18): yield 67 (crude) and 35% (purified); mp 188–204 °C; IR (KBr) 3060 (CH), 1590 (phenyl), 1545 (C=C), 1110 (CP), 760, 720, 695 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3, CH_3), 2.58 (brd t, 2, CH_2 at 4 position, $J_{HH} \simeq 10$ Hz), 3.75 (brd t, 2, CH_2 at 5 position, $J_{HH} \simeq 10$ Hz), 4.62 (brd s, 2, NCH_2Ph), 7.40 (s, 5, C_6H_5), 7.0–8.2 (m, 15, $P(C_6H_5)_3$); CIMS (isopentane) *m/e* (relative intensity) 434 (54.71, M^+).

[(*m*-Chlorobenzyl)-(6-phenyl-7-methyl-2*H*-1,3,4,7-tetrahydroazepin-2-ylidene)methyl]triphenylphosphonium Bromide (19): yield 64% (crude); mp 140–155 °C dec (purified); IR (KBr) 3200 (NH), 1625 (C=C), 1570 (NC=C), 1101 (CP), 757, 720, 692 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51 (d, 3, CH_3, $J_{HH} \simeq 7.8$ Hz), 1.4–2.1 (m, 2, CH_2), 2.4–3.0 (m, 2, CH_2), 3.96 (d, 2, CH_2Ar, $J_{PH} \simeq 20.4$ Hz), 5.1–5.7 (m, 2, =C(H)C and CHN), 6.7–8.3 (m, 24, aromatic H's), 8.65 (brd d, 1, NH, $J_{HH} \simeq 6$ Hz); FDMS *m/e* (relative intensity) 584 (100, M^+ from ^{35}Cl), 586 (61, M^+ from ^{37}Cl).

Anal. Calcd for $C_{39}H_{36}BrClNP \cdot H_2O$ (683.066): C, 68.58; H, 5.60. Found: C, 68.49; H, 5.48.

[(1-(*m*-Chlorobenzyl)-2,7-dimethyl-3-phenyl-1*H*-2,5-dihydroazepin-6-yl]triphenylphosphonium Bromide (20): yield 59% (crude); mp 140–160 °C dec (purified); IR (KBr) 3060, 3040, 2940 (CH), 1620 (C=C), 1600 (phenyl), 1530 (NC=C), 1101 (CP), 750, 715, 695 (phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, 3, CH_3, $J_{HH} \simeq 5.4$ Hz), 1.5–2.2 (m, 2, CH_2), 2.11 (s, 3, CH_3), 3.8 (brd s, 2, CH_2Ar), 4.8–5.2 (m, 1, CHN), 5.5–6.0 (m, 1, =C(H)C), 6.8–8.4 (m, 24, aromatic H's).

Anal. Calcd for $C_{39}H_{36}BrClNP \cdot H_2O$ (683.066): C, 68.58; H, 5.60. Found: C, 68.64; H, 5.40.

2-Methyl-3-(*m*-nitrobenzylidene)-1-pyrroline (21a). In a round-bottom flask fitted with a reflux condenser and an addition funnel was placed 1.00 g (2.36 mmol) of **14a**, 0.45 g (2.98 mmol) of *m*-nitrobenzaldehyde, and 10 mL of absolute ethanol. While stirring magnetically, 0.060 g (2.6 mmol) of sodium dissolved in 20 mL of absolute ethanol was added from the addition funnel over a 1-h period. After stirring at room temperature for 20 h, the volume was reduced (in vacuo) to approximately 2 mL and 100 mL of ethyl ether added. The resulting mixture (including the precipitate) was washed twice with 40 mL of water and then shaken for about 3 min with 50 mL of 10% HCl solution. The aqueous acid layer was washed successively with 50 mL of ethyl ether and 50 mL of ethyl acetate. The aqueous layer was basified with 20% sodium hydroxide solution (aqueous), and the resulting mixture (including the precipitate) was extracted with two 100-mL portions of ethyl ether. The combined ether extracts were dried (anhydrous $MgSO_4$) and filtered, and the ether was removed in vacuo to provide 0.43 g (84%) of crude product: mp 154–157 °C (after four recrystallizations from acetone–water); IR (KBr) 3100, 2920, 2850 (CH), 1600, 1590 (C=N, C=C), 1510, 1350 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (t, 3, CH_3, $J_{HH} \simeq 1.5$ Hz), 3.02 (td, 2, CH_2 at 4 position, $^tJ_{HH} \simeq 5.7$ Hz, $^dJ_{HH} \simeq 3$ Hz), 4.0–4.5 (m, 2, CH_2 at 5 position), 7.05 (t, 1, =C(H)Ar, $J_{HH} \simeq 3$ Hz), 7.7–8.9 (m, 4, $C_6H_4NO_2$); EIMS *m/e* (relative intensity) 216 (100 M^+).

Anal. Calcd for $C_{12}H_{12}N_2O_2$ (216.24): C, 66.65; H, 5.60. Found: C, 66.41; H, 5.49.

2-Methyl-1-(*o*-hydroxybenzylidene)-1-pyrroline (21b). Sodium hydride (57% mineral oil dispersion; 0.10 g, 2.38 mmol) and **14a** (1.00 g, 2.36 mmol) were stirred in 5 mL of dimethyl sulfoxide over nitrogen for 1 h. Salicylaldehyde (0.35 g, 2.87 mmol) was then added in one portion, and the mixture was stirred for approximately one day. The dark red solution was then poured into 100 mL of water and stirred vigorously. The resulting emulsion was extracted thrice with 100 mL of ethyl acetate, the extracts were dried (anhydrous $MgSO_4$), and the solvent was removed in vacuo. The residue was dissolved in a minimum quantity of hot benzene and allowed to cool overnight. Orange-yellow spines (0.11 g, 25%) were recovered by filtration after two recrystallizations from methanol–water: mp 195–198 °C; IR (KBr) 3070 (weak, H-bonded OH), 2940, 2880, 2860 (CH), 2600 (broad, $\geq N^+H$), 1600, 1590, 1575 (C=N, C=C, and phenyl), 1251 (C–O), 750 (phenyl) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.15 (t, 3, CH_3, $J_{HH} \simeq 1.5$ Hz), 2.6–3.0 (m, 2, CH_2 at 4 position), 3.7–4.1 (m, 2, CH_2 at 5 position), 6.7–7.9 (m, 6, =C(H)Ar, phenolic OH, or $\geq N^+H$ and aromatic H's); EIMS *m/e* (relative intensity) 187 (10.81, M^+), 186 (72.68, $M^+ - 1$).

Anal. Calcd for $C_{12}H_{13}NO$ (187.241): C, 76.98; H, 7.00. Found: C, 76.72; H, 7.11.

2,4-Dimethyl-3-phenyl-7-[2-(*m*-nitrophenyl)ethenyl]-2*H*-5,6-dihydroazepinium Chloride (22). A procedure similar to that used for the preparation of **21a** was employed with the following exceptions. After evaporating the ethanol solution to 1–2 mL and adding 50 mL of ethyl ether, the resulting mixture was washed twice with 20 mL of water. The ether layer was then placed in an Erlenmeyer flask with 25 mL of 10% hydrochloric acid, and the mixture was vigorously stirred for at least 15 min. The thick paste which formed was collected and triturated with 10 mL of ethanol. Filtration provided 0.10 g of crude product [29%; from 0.55 g (0.99 mmol) of **16a**, 0.03 g (1.33 mmol) of sodium, and 0.19 g (1.3 mmol) of *m*-nitrobenzaldehyde]. An analytical sample was obtained after three recrystallizations from ethanol–benzene: mp 210–220 °C dec; IR (KBr) 3040, 2960, 2930, 2860 (CH), 2600 (broad, N^+H), 1630 (C=N), 1615 (C=C), 1532, 1352 (NO_2), 832, 810, 795, 769, 738, 710 (aromatic) cm^{-1}; ^1H NMR ($CDCl_3$–CF_3CO_2H) δ 1.55 (d, 3, CH_3, $J_{HH} \simeq 7$ Hz), 1.65 (s, 3, CH_3), 2.87 (brd t, 2, CH_2, $J_{HH} \simeq 5.4$ Hz), 3.68 (d, 2, CH_2, $J_{HH} \simeq 5.4$ Hz), 5.1–5.7 (m, 1, CHN), 7.08–8.9 (m, 12, aromatic H's, HC=CH, and N^+H).

Anal. Calcd for $C_{22}H_{23}ClN_2O_2$ (382.889): C, 69.01; H, 6.05. Found: C, 69.14; H, 6.31.

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Registry No.——**1a**, 151-56-4; **1b**, 286-18-0; **1c**, 1499-00-9; **1d**, 51659-22-4; **2**, 2091-46-5; **3a**, 66966-54-9; **3b**, 66966-55-0; **3d**, 67011-18-1; **4a**, 66966-56-1; **4b**, 66966-57-2; **4c**, 66966-58-3; **5a**, 34387-64-9; **5b**, 54599-98-3; **6**, 66966-69-6; **7**, 66966-70-9; **8**, 66966-71-0; **9**,

66966-72-1; **10**, 66966-73-2; **13a**, 66966-74-3; **13b**, 66966-75-4; **14a**, 66966-59-4; **14b**, 66966-60-7; **15a**, 66966-76-5; **15b**, 60073-28-1; **15c**, 57291-16-4; **16a**, 66966-61-8; **16b**, 66966-62-9; **16c**, 66966-63-0; **17a**, 66966-65-2; **17b**, 66966-66-3; **17c**, 66966-67-4; **18**, 66966-77-6; **19**, 66966-64-1; **20**, 66966-68-5; **21a**, 66966-78-7; **21b**, 66966-79-8; **22**, 66966-80-1; azetidine, 503-29-7; piperidine, 110-89-4; dimethylamine HCl, 506-59-2; methylamine HCl, 593-51-1; aniline, 62-53-3; *m*-nitrobenzaldehyde, 99-61-6; salicylaldehyde, 90-02-8.

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Photochemistry of 2-Acetyl-3-phenylnorbornanes: Influence of a β-Phenyl Group on Carbonyl Reactivity in Relation to the Geometry of Both Chromophores

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The photochemistry of *trans*- and *cis*-2-acetyl-3-phenylnorbornanes *exo*-**3** and **5** and *endo*-**4** and -**6** has been investigated and compared to that of *exo*-acetylnorbornane (**1**) and the endo isomer **2**. The trans, exo compound **3** led exclusively to the Norrish type I photoproducts via the triplet state, while the cis isomer was inert. The endo compounds **4** and **6** underwent the type II photoelimination exclusively from the singlet state, and cyclization from both the singlet and the triplet. It has been shown that deactivation of excited states of carbonyl compounds by the phenyl group in both exo and endo isomers occurs only when the two chromophores are in the cis position.

The photoreactivity of formally nonconjugated phenylcarbonyl compounds has been the subject of some recent investigations.[1,2] Thus, it was shown by Whitten[2] that β-phenyl ketones with an available γ hydrogen undergo type II photoelimination as the only significant reaction. This author showed that while the triplet state is formed in good yields it returns exclusively to the ground state. The reaction occurs exclusively from the singlet state. The kinetic data obtained with somewhat rigid ketones allowed Whitten to suppose a through-space coupling between the two chromophores. Sauers,[3] studying the two isomeric 2-acetylbenzonorbornanes, reported that the exo isomer undergoes a nonefficient type I cleavage, while the endo isomer is photostable. The author suggested that the proximity of the two chromophores in the latter provides a channel for radiationless decay of the triplet.

It therefore appeared attractive to us to study rigid systems with an available γ hydrogen in order to investigate the influence of the phenyl group on carbonyl reactivity in relation to the relative geometry of both chromophores. Thus, the four isomeric acetylphenylnorbornanes **3**, **4**, **5**, and **6** were synthesized and their photochemical reactivity was compared to the acetylnorbornanes **1** and **2**. The photochemistry of the latter had not been studied before.

We report first that the behavior of the methyl ketones **1** and **2** was entirely different from that of the corresponding aryl ketones.[4] Secondly we show that the phenyl group exerts its influence only in the cis isomers **4** and **6**. Finally, we demonstrate that the Norrish type I reaction was more subject to the influence of the phenyl group than the γ hydrogen abstraction reaction.

Results

I. Product Study. The structures of the products were assigned on the basis of their spectral data and by chemical correlation in the case of ketone **13**.[5]

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