Table I. Preparation of Phosgene in Carbon Tetrachloride

catalyst	mol ratio cat./Cl_2	press of CO, atm	temp,[b] °C	time, min	yield[a] of $COCl_2$, %
$(n\text{-}C_4H_9)_3PO$ (1a)	1/50	60	rt	30	81
$(n\text{-}C_8H_{17})_3PO$ (1b)	1/57	60	rt	30	81
$(C_2H_5)_3PO$ (1c)	1/19	60	rt	40	69
$(C_6H_5)_3PO$ (1d)	1/50	60	rt	120	52
	0	60	rt	120	0
$(n\text{-}C_4H_9)_3PO$ (1a)	1/95	30	rt	135	96
	1/85	10	rt	195	80
	1/82	5	rt	360	84
	1/75	5	50	190	90

[a] Yields were based on chlorine, and the values are yields of *N,N'*-diphenylurea isolated in the treatment of the resultant phosgene solution with aniline and triethylamine and the subsequent separation of the products. [b] rt = room temperature.

catalytic effect of tertiary phosphine oxides and dichlorides for the reaction of chlorine and carbon monoxide in solution and a convenient preparative method of a phosgene solution, which is readily applicable even in the laboratory.

We recently reported the conversion of tertiary phosphine oxides (1) into tertiary phosphine dichlorides (2) by treatment with an equimolar amount of chlorine and pressurized carbon monoxide in carbon tetrachloride.[2] It is known that the reaction of 1 with phosgene gives 2,[3] but the formation of phosgene was not observed in a treatment of a solution of chlorine with carbon monoxide in the absence of 1 under the same conditions as in the transformation of 1 into 2.

We found that a catalytic amount of 1 promoted the reaction of chlorine with carbon monoxide in solution.

When a solution of chlorine in carbon tetrachloride was treated with pressurized carbon monoxide in the presence of a catalytic amount of tri-*n*-butylphosphine oxide (1a) at room temperature, an exothermic reaction occurred, giving phosgene as a solute in the solvent.

Tri-*n*-octylphosphine oxide (1b) also catalyzed the reaction for the production of phosgene, but triethylphosphine oxide (1c) and triphenylphosphine oxide (1d) were not so effective. The reaction rate depends remarkably on the kind of 1. Several experimental results are shown in Table I.

Since 1 is readily transformed into the corresponding 2 in the reaction system,[2] the reaction for the production of phosgene is catalyzed apparently by 2. 2 did not react with carbon monoxide in the absence of chlorine under the conditions applied for the phosgene formation.[4] In view of these facts, 2 seems to be not an intermediate but a catalyst.

The mechanism of these catalyses is not yet clear, but the catalytic effect is valuable since the quantitative conversion of chlorine into phosgene in solution became possible under mild conditions by the use of the catalyst 1.

Tetrachloroethane and *o*-dichlorobenzene could be used as the solvent in place of carbon tetrachloride.

The present preparative method of phosgene solution is very useful and has the following merits: (1) handling of highly toxic phosgene in the gaseous state can be avoided, since the greatest use of the reagent is done in solution, and (2) storage of highly toxic gas can be excluded, since the reagent can be produced only in a requisite amount just before use.

(2) M. Masaki and N. Kakeya, *Angew. Chem., Int. Ed. Engl.*, **16**, 552 (1977).

(3) G. Wunsch, K. Winterberger, and H. Geierhaas, *Z. Anorg. Allg. Chem.*, **369**, 33 (1966).

(4) The reaction of tertiary phosphine with phosgene is known to give 2 quantitatively: R. Appel, B. Blaser, and G. Siegemund, *Z. Anorg. Allg. Chem.*, **363**, 176 (1968).

Experimental Section

General Procedure for the Preparation of Phosgene. In an autoclave was placed a glass vessel containing a solution of 1a (0.72 g, 3.30 mmol) and chlorine (17.55 g, 247.53 mmol) in carbon tetrachloride (250 mL). The autoclave was pressurized with carbon monoxide to 5 kg/cm^2. The reaction mixture was stirred with a Teflon wing at 50 °C for 190 min, during which the pressure was maintained around 5 kg/cm^2 by intermittently supplying carbon monoxide. The autoclave was cooled to room temperature and then was brought to ordinary pressure. A colorless clear solution containing phosgene was obtained in the glass vessel. In order to determine the phosgene content, a solution of aniline (13.90 g, 149.24 mmol) and triethylamine (15.10 g, 149.18 mmol) in carbon tetrachloride (50 mL) was added to a portion (107.10 g) of the resultant solution (843.14 g) at 0 °C.

N,N'-Diphenylurea (5.99 g, 28.22 mmol) was separated from the resultant mixture by filtering followed by washing the collected crystalline product with water. The yield of *N,N'*-diphenylurea was 90%. This fact shows that the yield of phosgene in the solution obtained in the glass vessel was at least 90%.

Registry No. 1a, 814-29-9; 1b, 78-50-2; 1c, 597-50-2; 1d, 791-28-6; phosgene, 75-44-5; carbon monoxide, 630-08-0; chlorine, 7782-50-5.

Electronic Effects Exerted in the Thermolysis of 2-Oxetanone: Hammett Studies of the 3-Aryl and 4-Aryl Derivatives

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In spite of the widespread interest in the mechanism of the 2-oxetanone thermolysis,[1] only scanty reports describing the quantitative investigations of such reactions are available.[1b,e] As a result, the electronic effects exerted by the substituent at the C-3 or C-4 position have not yet been clarified.[2] Qualitatively, however, it has been fre-

(1) (a) A review: W. J. le Noble in "Studies in Organic Chemistry", Vol. 3, P. G. Gasman, Ed., Marcel Dekker, New York, N.Y., 1974, p 496. (b) T. L. James and C. A. Wellington, *J. Am. Chem. Soc.*, **91**, 7743 (1969). (c) W. T. Brady and A. D. Patel, *J. Org. Chem.*, **37**, 3536 (1972). (d) S. Mageswaran and M. U. S. Sultanbawa, *J. Chem. Soc., Perkin Trans. 1*, 884 (1976). (e) H. O. Krabbenhoft, *J. Org. Chem.*, **43**, 1305 (1978). For the stereospecific fragmentation of 2-oxetanones, see: (f) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966); (g) O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **90**, 2333 (1968); (h) W. Adam, J. Baeza, and J.-C. Liu, *ibid.*, **94**, 2000 (1972); (i) U. Schölkopf and I. Hoppe, *Angew. Chem., Int. Ed. Engl.*, **14**, 765 (1975); (j) J. Mulzer, A. Pointner, A. Chucholowski, and G. Brütrup, *J. Chem. Soc., Chem. Commun.*, 52 (1979). For the N and S analogue, see: (k) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Am. Chem. Soc.*, **92**, 1763 (1970); (l) F. Jung, N. K. Sharma, and T. Durst, *ibid.*, **95**, 3420 (1973).

(2) Qualitatively, it has been stated that electron-withdrawing substituent(s) at either C-3 or C-4 stabilizes the 2-oxetanones.[1c]

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Table I. Rate Constants of the Thermolysis of *trans*-3-Methyl-4-phenyl-2-oxetanone in Decane at 120 °C in the Presence of a Variety of Amines[a]

amine	mole ratio [amine]/[2-oxetanone]	10^5k_1, s^{-1}
$(C_2H_5)_3N$	1.1	4.39[b]
quinuclidine	1.0	4.32
TMED	0.10	4.57
TMED	0.54	4.39
TMED	1.0	4.34[c]
TMED	10.9	4.31
DABCO[d]	1.0	4.32

[a] The oxetanone concentration was (6.8-7.4) × 10^{-3} mol/L. [b] Use of a reaction vessel treated only with an aqueous solution of potassium hydroxide resulted in a k_1 of ca. 6.3 × 10^{-5} s^{-1}, with a downward drifting. [c] An average value of three runs. [d] 1,4-Diazabicyclo[2.2.2]-octane.

quently observed that certain 2-oxetanones cannot be isolated in pure form and that they fragment into carbon dioxide and an olefin.[1e-h] There must be, therefore, a sizable substituent effect on the stability of the 2-oxetanone. In this paper are reported quantitative studies of the thermolyses of two series of 2-oxetanones, namely, the 3-aryl-4,4-dimethyl (1) and 4-aryl-3,3-dimethyl derivatives (2), that were carried out to establish C-3 and C-4 substituent electronic effects. Interestingly, the aryl group at the C-4 position exerted considerable electronic influence on the rate, but that at the C-3 showed practically no effect.

Before carrying out the kinetic studies, we needed to establish reaction conditions which would yield reliable rate constants, because 2-oxetanones are, in general, very sensitive toward acidic impurities in the reaction system. The most acid sensitive of all the 2-oxetanones yet examined in related studies is *trans*-3-methyl-4-phenyl-2-oxetanone, and hence this oxetanone was examined under a variety of conditions. After extensive investigations, we settled upon the following conditions: reactions were run (1) in a repeatedly base-treated vessel, (2) in decane (base-washed and freshly distilled), (3) with an oxetanone concentration of ca. 10^{-2} mol/L, (4) in the presence of an equimolar amount of *N,N,N',N'*-tetramethylethylenediamine (TMED), and (5) under an argon atmosphere. In particular, the addition of tertiary amine was essential. The possibility that TMED disturbed the kinetics was ruled out from the following observations. (1) The rate constant obtained in the presence of the tertiary amine was smaller than that in its absence. (2) The changes in either the concentration of TMED or the kind of tertiary amine (TMED, DABCO, triethylamine, or quinuclidine) resulted in virtually no influence on the rate constant (Table I). (3) The thermolysis was regiospecifically quantitative in all cases; no amine-incorporated product was detected.

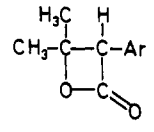
Since the fragmentation was strictly regiospecific and quantitative, the rates of the reaction were determined by monitoring the amount of produced styrene by UV spectrometry. The reaction obeyed a first-order rate law up to 80% completion. The resultant rate constants are summarized in Table II.

The Hammett treatment of the 4-aryl series (2) gave a good correlation with σ^+.[3] The reaction constant is rather large (ρ = −1.52, r = 0.998).[4] On the other hand, only a fair correlation was obtained in the 3-aryl series (1), and all the compounds gave nearly the same rate constants: ρ = +0.03 (r = 0.615). Evidently, significant positive charge develops at the C-4, but not at the C-3, in the activated complex. If it is assumed that the charge development is associated with the magnitude of the stretching of the bond, the 1,4 bond of the 2-oxetanone ring will be stretched to a considerable extent, but only a minor degree of stretching will occur at the 2,3 bond. Such unequal stretching may suggest stepwise heterolytic fragmentation; the magnitude of the reaction constants, which are more or less similar to those observed in the olefin-forming pyrolysis of esters,[5] and the well-documented stereospecificity of the fragmentation[1a,d,f-j,6] suggest that a concerted reaction via a quasi-zwitterionic transition state (3)[7] is highly probable.

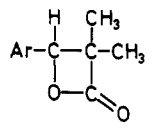
Table II. Rate Constants of the Thermolysis of 3-Aryl-4,4-dimethyl-2-oxetanone (1) and 4-Aryl-3,3-dimethyl-2-oxetanone (2) in Decane at 150 °C

2-oxetanone	10^5k_1,[a] s^{-1}	2-oxetanone	10^5k_1,[a] s^{-1}
p-$CH_3OC_6H_4$-1	25.0, 24.9	*p*-$CH_3C_6H_4$-2	6.72, 6.66
p-$CH_3C_6H_4$-1	24.2, 23.8	C_6H_5-2	1.81, 1.80
C_6H_5-1	23.9, 23.7	*p*-ClC_6H_4-2	1.46, 1.40
p-ClC_6H_4-1	27.1, 27.2	*m*-ClC_6H_4-2	0.489, 0.496
m-ClC_6H_4-2	27.0, 26.7	*p*-$NO_2C_6H_4$-2	0.148[b]

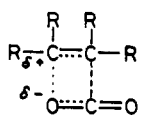
[a] The probable error was less than 1.5% in most cases. The reaction constants obtained in the plot against σ^+ were +0.03 (r = 0.615) for 1 and −1.52 (r = 0.998) for 2. [b] Extrapolated from the rate constants at higher temperatures: 1.16 × 10^{-5} s^{-1} at 170 °C, 4.37 × 10^{-5} s^{-1} at 185 °C, and 1.76 × 10^{-4} s^{-1} at 200 °C; $\Delta H^{\ddagger}$ = 36.9 kcal/mol, $\Delta S^{\ddagger}$ = +1.3 eu.



1



2



3

Experimental Section

UV spectra were recorded on a Cary Model 17 spectrophotometer. IR spectra were taken on a Hitachi Model 215 grating spectrophotometer. NMR spectra were obtained with a JEOL PS-100 spectrometer; chemical shifts are given in parts per million from tetramethylsilane. GC was done on a Hitachi 063 gas chromatograph and high-pressure LC on a Hitachi Model 635 liquid chromatograph. Microanalyses were carried out by the Microanalytical Laboratory, Faculty of Pharmaceutical Science of Hokkaido University. Melting points are uncorrected.

2-Oxetanones. The 2-oxetanones were prepared from the corresponding 3-hydroxypropionic acid according to the methods described by Adam, Baeza, and Liu.[1h] 3-*p*-Anisyl-4,4-dimethyl-2-oxetanone was a labile oil, which could be purified to an analytically pure state only by rapid distillation after a brief purification by Florisil column chromatography: bp 80–90 °C (bath temperature) (<10^{-4} mm); n^{25}_D 1.5178; IR (thin film) 1810 cm^{-1}; NMR (CCl_4) δ 1.14 (s, 3 H), 1.68 (s, 3 H), 3.74 (s, 3 H), 4.43 (s, 1 H), 6.78 (d, J = 9 Hz, 2 H), 7.02 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.65; H, 6.85.

(3) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); **80**, 4979 (1958).

(4) A ρ value of −3.07, based only on the H, *m*-Cl, and *p*-Cl derivatives, has been reported for the thermolysis of 4-aryl-3,3-dichloro-2-oxetanones.[1e]

(5) In ester pyrolyses, ρ values of −0.6 to −0.7 have been reported for >CHC(Ar)(OCOCH$_3$)−, whereas small positive values (0.08 to <0.3) have been obtained in >CH(Ar)CH(OCOCH$_3$)− type compounds (R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Am. Chem. Soc.*, **84**, 4817 (1962); G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, **34**, 2090 (1969)). For other ρ values of seemingly concerted reactions, see G. G. Smith and F. W. Kelly, *Prog. Phys. Org. Chem.*, **8**, 75 (1971).

(6) We also observed that the thermolysis of *cis*-3-*tert*-butyl-4-phenyl-2-oxetanone was strictly regiospecific and stereospecific to produce *cis*-2-*tert*-butylstyrene.

(7) K. W. Egger, *J. Am. Chem. Soc.*, **95**, 1745 (1973).

The remaining 2-oxetanones gave the following data.

3-*p*-Tolyl-4,4-dimethyl-2-oxetanone: mp 40–42 °C (pentane–ether, 6:1); IR (KBr) 1800 cm^{-1}; NMR (CCl_4) δ 1.15 (s, 3 H), 1.70 (s, 3 H), 2.34 (s, 3 H), 4.45 (s, 1 H), 6.9–7.2 (m, 4 H). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.90; H, 7.53.

3-Phenyl-4,4-dimethyl-2-oxetanone has been reported in the literature[8] but no details are given: mp 53–54 °C; IR (KBr) 1805 cm^{-1}; NMR (CCl_4) δ 1.15 (s, 3 H), 1.72 (s, 3 H), 4.54 (s, 1 H), 7.0–7.5 (m, 5 H). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.97; H, 6.90.

3-(*p*-Chlorophenyl)-4,4-dimethyl-2-oxetanone: mp 60.5–62.5 °C (pentane–ether, 10:1); IR (KBr) 1805 cm^{-1}; NMR (CCl_4) δ 1.18 (s, 3 H), 1.74 (s, 3 H), 4.51 (s, 1 H), 7.15 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26; Cl, 16.83. Found: C, 62.77; H, 5.29; Cl, 16.94.

3-(*m*-Chlorophenyl)-4,4-dimethyl-2-oxetanone: oil, bp 80–85 °C (bath temperature) ($<10^{-4}$ mm); n^{25}_D 1.5242; IR (thin film) 1815 cm^{-1}; NMR (CCl_4) δ 1.21 (s, 3 H), 1.75 (s, 3 H), 4.53 (s, 1 H), 7.0–7.4 (m, 4 H). Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26; Cl, 16.83. Found: C, 62.85; H, 5.28; Cl, 16.69.

4-*p*-Tolyl-3,3-dimethyl-2-oxetanone: mp 61.0–62.5 °C (pentane–ether, 10:1); IR (KBr) 1820, 1810 cm^{-1}; NMR (CCl_4) δ 0.84 (s, 3 H), 1.51 (s, 3 H), 2.39 (s, 3 H), 5.15 (s, 1 H), 7.10 (s, 4 H). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.57; H, 7.58.

4-Phenyl-3,3-dimethyl-2-oxetanone: mp 25.0–26.5 °C (pentane–ether, 10:1) (reported as an oil);[1h] IR (KBr) 1820 cm^{-1}; NMR (CCl_4) δ 0.84 (s, 3 H), 1.53 (s, 3 H), 5.18 (s, 1 H), 7.0–7.6 (m, 5 H). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.99; H, 7.00.

4-(*p*-Chlorophenyl)-3,3-dimethyl-2-oxetanone: mp 68–70 °C (pentane–ether, 4:1); IR (KBr) 1825, 1815 cm^{-1}; NMR (CCl_4) δ 0.87 (s, 3 H), 1.54 (s, 3 H), 5.16 (s, 1 H), 7.16 (d, J = 9 Hz, 2 H), 7.32 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26; Cl, 16.83. Found: C, 62.98; H, 5.35; Cl, 16.70.

4-(*m*-Chlorophenyl)-3,3-dimethyl-2-oxetanone: oil, bp 80 °C (bath temperature) ($<10^{-4}$ mm); n^{25}_D 1.5237; IR (thin film) 1830 cm^{-1}; NMR (CCl_4) δ 0.89 (s, 3 H), 1.56 (s, 3 H), 5.16 (s, 1 H), 7.0–7.4 (m, 4 H). Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26; Cl, 16.83. Found: C, 62.66; H, 5.31; Cl, 16.94.

4-(*p*-Nitrophenyl)-3,3-dimethyl-2-oxetanone: mp 62.5–64.0 °C (pentane–ether, 1:2); IR (KBr) 1825, 1840 cm^{-1}; NMR (CCl_4) δ 0.88 (s, 3 H), 1.61 (s, 3 H), 5.34 (s, 1 H), 7.44 (d, J = 9 Hz, 2 H), 8.19 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{11}H_{11}O_4N$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.75; H, 4.81; N, 6.39.

trans-3-Methyl-4-phenyl-2-oxetanone: mp 26–29 °C (contaminated by ca. 3% of *trans*-1-phenylpropene); n^{25}_D 1.5223; IR (thin film) 1825 cm^{-1}; NMR (CCl_4) δ 1.53 (d, J = 7.5 Hz, 3 H), 3.48 (d of q, J = 4.3 and 7.5 Hz, 1 H), 5.04 (d, J = 4.3 Hz, 1 H), 7.36 (s, 5 H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.26; H, 6.25. Attempts to prepare 4-*p*-anisyl-3,3-dimethyl-2-oxetanone have been unsuccessful.

Products. GC analysis proved that the production of the olefin was quantitative in all cases. All olefins are known compounds,[9] and hence they were characterized by spectral examinations.

Kinetics Procedures. Decane was purified by successive washings with fuming sulfuric acid, water, and a 10% aqueous solution of sodium hydroxide. It was then dried over potassium hydroxide pellets and finally distilled over lithium aluminum hydride, bp 60–61 °C (13 mm). The reaction vessel was treated with a 10% aqueous solution of potassium hydroxide at 100 °C for 7 h. It was then rinsed with many portions of water and, after drying, treated with a 0.7 M solution of TMED in decane at 140 °C for more than 8 h. The vessel was then rinsed with several portions of decane and used immediately.

A soluton of an equimolar mixture of 2-oxetanone [(7–9) × 10^{-3} mol/L] and TMED in decane was prepared in the reaction vessel under an argon atmosphere. Argon was bubbled through the solution for 30–60 min, and then the reaction was started by soaking the vessel in a constant-temperature bath. At appropriate time intervals, an aliquot of 30–50 μL of the solution was withdrawn from the vessel by means of a glass capillary tube. Exactly 20 μL of the solution was then taken from the each aliquot with a microsyringe and diluted to 3 mL with hexane. The progress of the reaction was followed by measuring the absorbance at the UV maximum of the produced styrene: 252 nm for *p*-anisyl, 247 nm for *p*-tolyl, 244 nm for phenyl, 251 nm for *p*-chlorophenyl, 248 for *m*-chlorophenyl, and 303 for *p*-nitrophenyl. The reproducibility of this sampling technique was more than 99.8%. All glassware used in these procedures was pretreated with base and dried.

For the *p*-nitrophenyl derivative, the parent 2-oxetanone absorbed strongly at 260 nm. However, the absorbance at 303 nm was only 4% of that of the styrene produced, and hence the kinetic measurement was not disturbed. In order to check this point further, we followed the rate of the reaction by monitoring the amount of the oxetanone by liquid chromatography (3040 column, UV detector at 250 nm, hexane–ether (2:1), 0.8 mL/min). The rate constants thus determined were essentially the same as those obtained by the standard procedures; k_1 at 170 °C was (1.16 ± 0.04) × 10^{-5} s^{-1} and k_1 at 200 °C was (1.77 ± 0.14) × 10^{-4} s^{-1}.

In order to examine the effect of the TMED equation on the rate constant, we studied the rate of the reaction of *trans*-3-methyl-4-phenyl-2-oxetanone under a variety of conditions. The results are summarized in Table I.

Registry No. **1** (Ar = *p*-$CH_3OC_6H_4$), 71155-74-3; **1** (Ar = *p*-$CH_3C_6H_4$), 71155-75-4; **1** (Ar = C_6H_5), 57015-11-9; **1** (Ar = *p*-ClC_6H_4), 71155-76-5; **1** (Ar = *m*-ClC_6H_4), 71155-77-6; **2** (Ar = *p*-$CH_3C_6H_4$, 71155-78-7; **2** (Ar = C_6H_5), 35947-70-7; **2** (Ar = *p*-ClC_6H_4), 71155-79-8; **2** (Ar = *m*-ClC_6H_4), 71155-80-1; **2** (Ar = *p*-$NO_2C_6H_4$), 71155-81-2; *trans*-3-methyl-4-phenyl-2-oxetanone, 71155-82-3; *p*-anisylethene, 637-69-4; *p*-tolylethene, 622-97-9; styrene, 100-42-5; *p*-chlorophenylethene, 1073-67-2; *m*-chlorophenylethene, 2039-85-2; *p*-nitrophenylethene, 100-13-0; $(C_2H_5)_3N$, 121-44-8; quinuclidine, 100-76-5; TMED, 110-18-9; DABCO, 280-57-9.

(8) U. Schölkopf and I. Hoppe, *Angew. Chem., Int. Ed. Engl.*, **14**, 765 (1975).

(9) A. Sosa, *Ann. Chim. (Paris)*, **14**, 5, 73, 74 (1940); M. G. Voronkov, A. S. Broun, and B. B. Karpenko, *Zh. Obshch. Khim.*, **19**, 1927, 1934 (1949); C. E. Boord, A. L. Henne, K. W. Greenlee, W. L. Perilstein, and J. M. Derfer, *Ind. Eng. Chem.*, **41**, 609 (1949); G. G. S. Dulton, T. I. Briggs, and E. Merler, *Can. J. Chem.*, **31**, 1138 (1953); O. Rüchardt, *Chem. Ber.*, **94**, 2609 (1961); C. Rüchardt and S. Eichler, *ibid.*, **95**, 1921 (1962); H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965).

A Simple Approach to 1-Azaspiro[4.5]decanes

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1-Aza[*n*.5]spiranes have recently attracted considerable attention because they are present in various natural products such as the cephalotaxus alkaloids[2] and histrionicotoxine groups.[3] We now report a novel route to spiro heterocyclic compounds in a one-pot reaction from enamines and their α-bromo iminium salts.

We have previously reported that α-bromo iminium salts **2**, readily prepared by bromination of parent enamines, undergo enolization[4] to the β-halo enamine **3** and a competing addition reaction[5] (Scheme I). In the latter

(1) Taken, in part, from a thesis submitted by J.-M.P. to the University of Rouen, June 1978.

(2) S. W. Weinreb and M. F. Semmelhack, *Acc. Chem. Res.*, **8**, 158 (1975).

(3) (a) J. W. Daly, I. Karle, C. W. Meyers, T. Tokuyama, J. A. Waters, and B. Witkop, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 1870 (1971); (b) T. Tokuyama, K. Uenoyama, G. Brown, J. W. Daly, and B. Witkop, *Helv. Chim. Acta*, **57**, 2597 (1974).

(4) L. Duhamel, P. Duhamel, and J.-M. Poirier, *Tetrahedron Lett.*, 4237 (1973).

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