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

Lucette Duhamel* and Jean-Marie Poirier[1]

Laboratoire de Chimie Organique, Faculté des Sciences et des Techniques de Rouen, 76130 Mont Saint Aignan, France

Pierre Granger

Service Commun RMN, Université de Rouen, 76130 Mont Saint Aignan, France

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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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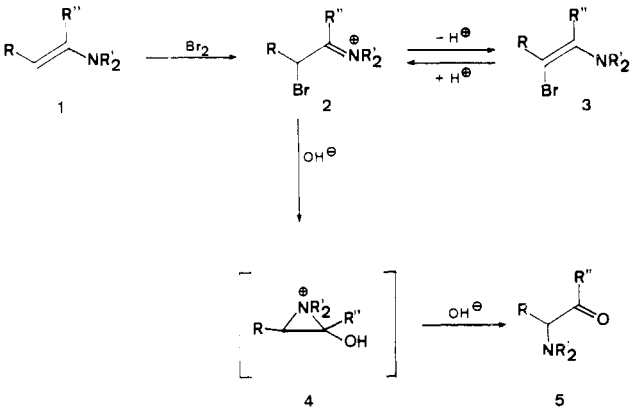
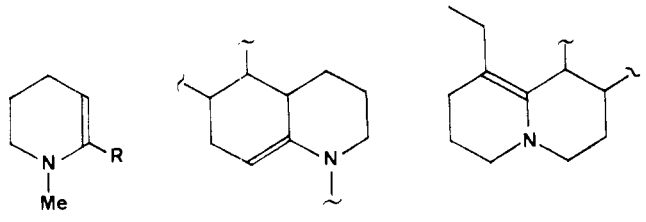
Scheme I



case, bromine is substituted by the NR'_2 group, producing via aziridinium salt 4 the rearranged amino compound 5 when the nucleophilic reagent is hydroxide ion.

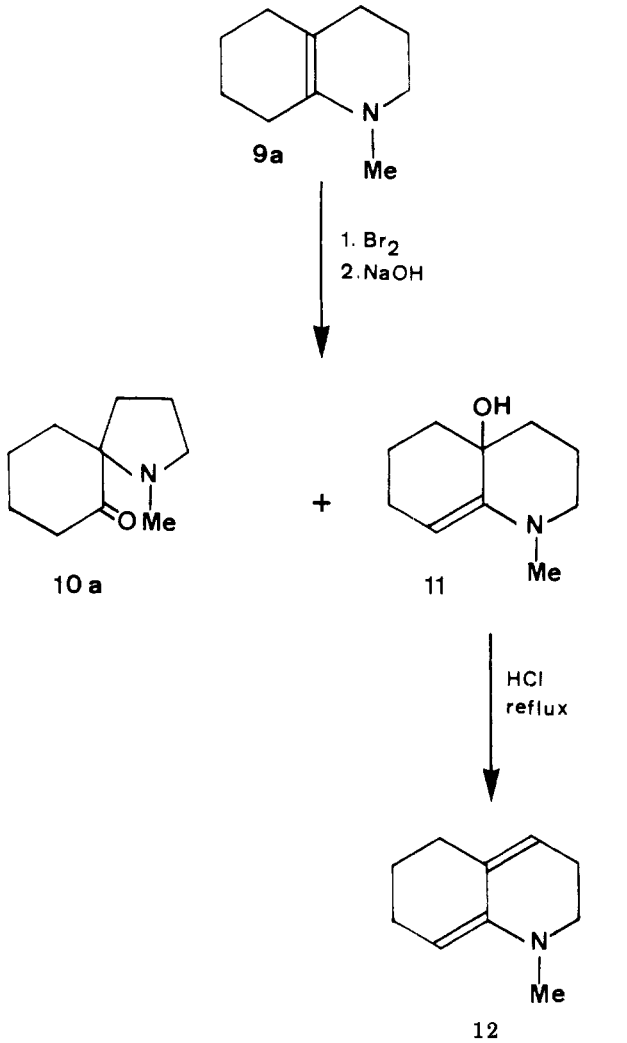
The reaction 1 → 2 → 5 when applied to monoheterocyclic compounds 6 has given a contraction of the



heterocyclic ring.[6] With the bicyclic compounds 7[7] and 8[8] two types of rearranged product have been observed: for the first compound, expansion of the heterocyclic ring and for the second, ring expansion and contraction.

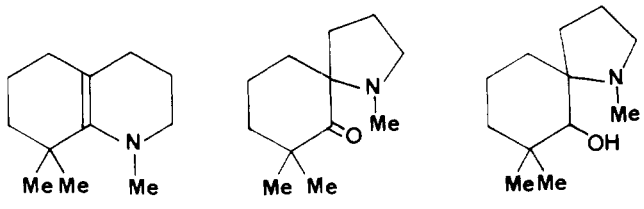
For bicyclic enamines in which the double bond is common to the two rings, our previous work[1,5,6] suggested a new route to functionalized 1-azaspiro compounds by a ring-contraction reaction. This paper describes our investigation in this field with starting enamines **9a** and **9b**. Bromine and aqueous NaOH were successively added to enamine **9a**.[9] This treatment afforded 1-azaspiro compound **10a**.[10] However, the major product was enamine **11**. **10a** and **11** were obtained in a 20/80 ratio (Scheme II). The structure of enamine **11** was established by comparison with an authentic sample prepared from 1-methyldecahydroquinoline.[11] We observed that enamine **11** underwent rapid transformation into diene **12** by refluxing in concentrated hydrochloric acid (Scheme II). The structure of diene **12** was assigned on the basis of ^1H NMR data with the aid of proton–proton spin decoupling. Acidic treatment of the mixture of spiro compound **10a** and enamine **11** provided unchanged **10a** and diene **12** which

Scheme II



could be readily separated by column chromatography.

In order to favor the formation of the spiro compound, we prepared enamine **9b**, in which enolization is blocked.



Enamine **9b** treated as described above for enamine **9a** underwent ring contraction to afford only the 1-azaspiro compound **10b** (crude yield 70%, distilled yield 58%). As might be expected, spiro ketone **10b** can be easily reduced to spiro amino alcohol **13** by lithium aluminum hydride.

Structures of spiro compounds **10a** and **10b** were established from ^1H and ^{13}C NMR data. ^{13}C NMR data are presented in Table I.

For ^{13}C resonances, the undecoupled spectra allowed us to assign immediately the different methyl lines. Previous work on spiro compounds and cyclohexanones[12,13] has led to the assignment of C_6, C_7, C_8, and C_9. The difference of chemical shifts for this last carbon between **10a** and **10b**

(5) (a) P. Duhamel, L. Duhamel, C. Collet, and A. Haïder, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **273**, 1461 (1971); (b) L. Duhamel, P. Duhamel, C. Collet, A. Haïder, and J.-M. Poirier, *Tetrahedron Lett.*, 4743 (1972).

(6) L. Duhamel and J.-M. Poirier, *Tetrahedron Lett.*, 2437 (1976).

(7) M. Takeda, H. Inoue, M. Konda, S. Saito and H. Kugita, *J. Org. Chem.*, **37**, 2677 (1972).

(8) (a) C. Costa, H. Criche, and P. Husson, *Tetrahedron*, 315 (1977); (b) A. Buzas, C. Retourne, J. P. Jacquet, and G. Lavielle, *Heterocycles*, **6**, 1037 (1977).

(9) Enamine **9a** was prepared by the method of Evans: D. A. Evans, *J. Am. Chem. Soc.*, **92**, 7593 (1970); D. A. Evans and L. A. Domeier, *Org. Synth.* **54**, 93 (1974).

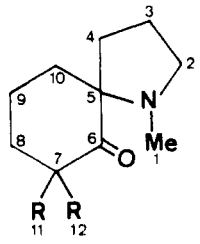
(10) This compound was also prepared by another way in our laboratory: M. Kotera, unpublished results.

(11) N. J. Leonard, L. A. Miller, and P. D. Thomas, *J. Am. Chem. Soc.*, **78**, 3463 (1956). In this reaction which gave **11** and unchanged starting material, the authors suggested **9a** as a transition step. We have examined this possibility and have prepared **11** from **9a** with higher yield (distilled yield 75%).

(12) D. Zimmermann, R. Ottinger, J. Reisse, H. Christol, and J. Brugidou, *Org. Magn. Reson.*, **6**, 346 (1974).

(13) J. B. Stothers and C. T. Tan, *Can. J. Chem.*, **52**, 308 (1974).

Table I. ^{13}C NMR Chemical Shifts[a] and Positional Assignments of Spiro Compounds



10a R = H

10b R = Me

position	10a δ	10b δ	10b J_{C-H}, Hz
1	34.27 q	34.76 q	133.5
2	53.25 t	53.72 t	135.7
3	21.01 t	22.07 t	132.1
4	33.23 t	33.59 t	132.5
5	77.23 s	72.04 s	
6	211.9 s	217.49 s	
7	40.51 t	45.50 s	
8	26.02 t	39.22 t	130.5
9	22.90 t	19.22 t	132
10	31.51 t	37.67 t	133
11		26.80 q	127.3
12		27.06 q	127.3

[a] Chemical shifts are relative to tetramethylsilane as an internal standard.

is similar to that obtained on other spiro compounds when two methyl groups are α to the CO. The only remaining singlet in the undecoupled spectra was C_5 which is more deshielded than in known cases[12] with cyclopentanes where the spirocarbon is at about 57 ppm. But for C_5, the passage from cyclopentane to pyrrolidine increases the ^{13}C chemical shift by about 30 ppm which explains our results. Use of the spiro effect[12] on the pyrrolidine ring allows the assignments of the last carbons, C_2, C_3, and C_4.

Experimental Section

General Procedures. All boiling points are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer 377 spectrophotometer (thin film unless otherwise noted). Ultraviolet spectra (UV) were recorded on a Beckman DB spectrophotometer. ^1H NMR spectra were determined on a Perkin-Elmer R 12 or a Bruker WH-90 D spectrometer, and ^{13}C NMR spectra on a Bruker WH-90 D spectrometer. The chemical shifts (δ values) are given in parts per million relative to Me_4Si as an internal standard in $CDCl_3$ solutions. Couplings (J) are in hertz (Hz). Gas chromatography/mass spectra[14] were obtained on a JEOL D 100 instrument, with GC data determined on a Girdel 75-E1 gas chromatograph with a 5% SE-30 column.

1,8,8-Trimethyl-Δ⁹-octahydroquinoline (9b). To 4.16 g (30 mmol) of 2,2-dimethylcyclohexylidene-*N*-methylimine[15] was added ethylmagnesium bromide (18.5 mL of a 1.8 M THF solution). The reaction mixture was heated with reflux until 1 equiv of gas had been formed[16] (about 5 h). After the mixture had cooled to room temperature, 5 g of 1-bromo-3-chloropropane (32 mmol) was added dropwise, and the solution was refluxed with 3 g of triethylamine (30 mmol) during 7 h and then allowed to stand overnight at room temperature. The reaction mixture was quenched with 5% aqueous sodium hydroxide, extracted with diethyl ether, and then dried ($MgSO_4$) and distilled, leaving 3.17 g (59%) of enamine **9b**: bp 64 °C (0.35 mm); IR 1640 cm^{-1}; ^1H NMR δ 2.80 (m, 2 H), 2.52 (s, 3 H), 2.05–1.45 (m, 10 H), 1.12 (s, 6 H).

Anal. Calcd for $C_{12}H_{21}N$: C, 80.45; H, 11.73; N, 7.82. Found: C, 80.45; H, 11.7; N, 7.7.

6-Oxo-1,7,7-trimethyl-1-azaspiro[4.5]decane (10b). To a stirred solution of 2.86 g of enamine **9b** (16 mmol) in 60 mL of dry ether was added at −70 °C 2.56 g of bromine (16 mmol) in 50 mL of dry cold (about −60 °C) ether. After the addition was complete, the suspension of the α-bromo iminium salt was allowed to warm to room temperature. The yellow reaction mixture was cooled to −20 °C and 20 mL of 20% aqueous sodium hydroxide was added dropwise, while stirring. The reaction mixture was stirred for 1 h and then stored 48 h at −18 °C. After the reaction mixture was warmed to room temperature, it was extracted with ether and the extract was dried ($MgSO_4$) (crude yield 70%) and distilled to give 1.81 g (58%) of **10b**: bp 79 °C (0.65 mm); IR 1695 cm^{-1}; ^1H NMR δ 2.92 (m, 2 H), 2.27 (s, 3 H), 1.92–1.62 (s, 10 H), 1.12 (s, 3 H), 1.07 (s, 3 H).

Anal. Calcd for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.5; H, 11.0; N, 7.1.

1-Methyl-6-oxo-1-azaspiro[4.5]decane (10a) and 1-Methyl-Δ⁴,Δ⁸-hexahydroquinoline (12). The treatment was the same as described above for enamine **9b**. After evaporation the reaction mixture (20% spiro compound **10a** and 80% enamine **11**; crude yield 74%) was refluxed for 10 min with 10 mL of concentrated hydrochloric acid. Two components, diene **12** and unchanged **10a**, were separated by liquid chromatography on alumina, using pentane-ether (9/1) as eluent. Spiro compound **10a**: isolated yield based on enamine **9a**, 9%; IR ($CDCl_3$) 1705 cm^{-1}; ^1H NMR δ 2.90 (m, 2 H), 2.43 (s, 3 H), 1.9–1.4 (m, 12 H). Diene **12**: yield based on enamine **9a**, 52%; bp 70 °C (0.45 mm); IR 1600 cm^{-1}; UV (cyclohexane) λ_{max} 237 nm (ϵ 3.2 × 10^3), λ_{max} 224 nm (ϵ 8.4 × 10^3); ^1H NMR δ 5.45 (m, 1 H), 4.70 (t, 1 H, J = 1.6 Hz), 2.84 (t, 2 H), 2.60 (s, 3 H), 2.25 (m, 6 H), 1.60 (m, 3 H). When diene **12** was prepared from pure enamine **11** (obtained from **9a**[11]) the distilled yield was 75%.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.53; H, 10.07; N, 9.40. Found: C, 80.4; H, 10.2; N, 9.7.

6-Hydroxy-1,7,7-trimethyl-1-azaspiro[4.5]decane (13). To a suspension of 0.3 g of lithium aluminum hydride in 25 mL of dry ether was added dropwise 1.1 g of spiro compound **10b** (5.65 mmol) at 0–5 °C. The reaction mixture was allowed to warm to room temperature, while stirring, for 2 h and then quenched with ammonium chloride (saturated aqueous solution), extracted with ether, dried ($MgSO_4$), and distilled, leaving 0.65 g (58%) of **13**: bp 75 °C (0.5 mm); IR 3490 cm^{-1}; ^1H NMR δ 3.15 (s, 1 H), 3.0 (m, 1 H), 2.65 (m, 2 H), 2.22 (s, 3 H), 2.84–1.73 (m, 10 H), 1.04 (s, 3 H), 0.90 (s, 3 H).

Anal. Calcd for $C_{12}H_{23}NO$: N, 7.10. Found: N, 7.0.

Acknowledgment. We are indebted to Rhone-Poulenc for financial support.

Registry No. 9a, 33768-69-3; **9b**, 71032-68-3; **10a**, 71032-69-4; **10b**, 71032-70-7; **11**, 71032-71-8; **12**, 71032-72-9; **13**, 71032-73-0; 2,2-dimethylcyclohexylidene-*N*-methylamine, 71032-74-1; 1-bromo-3-chloropropane, 109-70-6.

(14) Identification by GC/MS confirmed the structural assignments, in addition to the NMR data.

(15) This imine was prepared from 2,2-dimethylcyclohexanone by the method of H. Weingarten, J. P. Chupp, and W. A. White, *J. Org. Chem.*, **32**, 3246 (1967).

(16) G. Stork and S. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).

Dehydration of Ketones to Acetylenes

James J. Harrison

Gulf Research & Development Company, P.O. Drawer 2038, Pittsburgh, Pennsylvania 15230

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A potentially important synthetic transformation is the conversion of a ketone to an acetylene by dehydration (eq 1). This energetically unfavorable process (by 33.5 kcal/mol)[1] is highly desirable because, in principle, acetylenes can be produced from readily available starting materials in one step. Previously, acetylenes generally have

(1) Heat of formation data were obtained for acetophenone, water, and phenylacetylene from D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969.

0022-3263/79/1944-3578$01.00/0