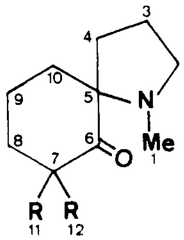
Table I. ^{13}C NMR Chemical Shifts[a] and Positional Assignments of Spiro Compounds



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. ^{1}H 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-Δ^9-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}; ^{1}H 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}; ^{1}H 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-Δ^4,Δ^8-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}; ^{1}H 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); ^{1}H 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}; ^{1}H 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.

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[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

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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

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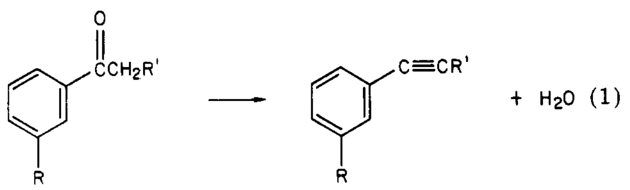
[1] Heat of formation data were obtained for acetophenone, water, and phenylacetylene from D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969.



1a, R = H; R' = H
b, R = NO_2; R' = H
c, R = NH_2; R' = H
6a, R = H; R' = CH_3

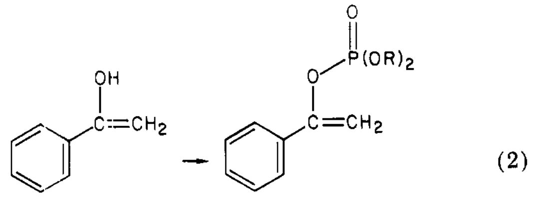
2a, R = H; R' = H
b, R = NO_2; R' = H
c, R = NH_2; R' = H
6b, R = H; R' = CH_3

been synthesized by multistep processes.[2] Acetylenes have recently found widespread importance in olefin synthesis[3] and as prepolymers for heat stable resins.[4]

We would like to report a one-step thermal dehydration[5] of ketones to acetylenes. The thermal reactions of ketones in general produce products derived from carbon monoxide loss and radical recombinations.[6,7] We observe that acetophenone (**1a**) produces phenylacetylene (**2a**) when flash distilled through a hot tube containing either phosphorus pentoxide or the solid commercial phosphoric acid catalyst UOP No. 1.[8] The pyrolysis over UOP No. 1 was examined in some detail and our results are reported in Table I. The yield of acetylene is not high but recycling the starting ketone may be possible.

The pyrolysis is quite clean. The only observable volatile products were unreacted acetophenone, phenylacetylene, and water. The yield of phenylacetylene was observed to increase with increasing temperature and with decreasing pressure. The dehydrating agent, UOP No. 1, became discolored during each pyrolysis and a brown acidic material, probably a condensed phosphoric acid residue, was formed in the exit side of our pyrolysis tube. Recycle of UOP No. 1 resulted in rapid deterioration in the phenylacetylene yield. This suggests that the reaction is not a simple acid-catalyzed dehydration, and that UOP No. 1 is not acting in a catalytic fashion.

Instead the reaction may proceed through the initial formation of a vinyl phosphate (**3**), which may form from the enol form of acetophenone (**4**) and the phosphoric anhydride (eq 2). Thermally induced elimination of a phosphoric acid from **3** could then produce phenylacetylene. To investigate this possibility, we have independently synthesized the vinyl phosphate (**5**) by the Perkow reaction[9] of phenacyl chloride and triethyl phosphite. Under conditions similar to those of our thermal dehydration, **5** produced only acetophenone. This indicates that a trisubstituted orthophosphate such as **5** cannot be an intermediate in the reaction.



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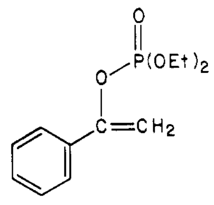

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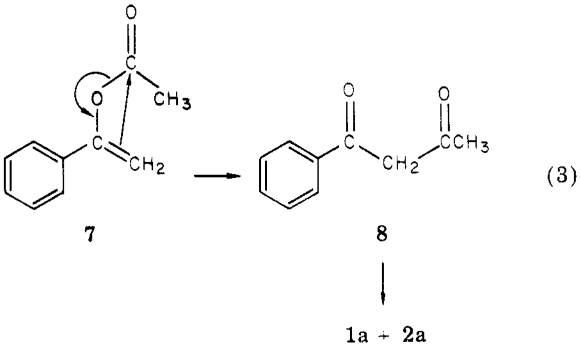
Substituted acetophenones such as *m*-nitro (**1b**) or *m*-aminoacetophenone (**1c**) when pyrolyzed with UOP No. 1 failed to give the desired acetylenes **2b** and **2c**, respectively, but instead formed a polymeric material on the walls of the pyrolysis tube. Propiophenone (**6a**) under dehydration conditions produced a C_9H_9 hydrocarbon in 43% yield which was identified as 1-phenyl-1-propyne (**6b**) (GC and NMR comparison with an authentic sample).

The pyrolysis of acetophenone enol acetate (**7**) has also been examined. In the absence of any catalyst at 650 °C, the major product is 1-phenyl-1,3-butanedione (**8**).[11] This process has been shown to be intramolecular and nonheterolytic in nature[11] (eq 3). Above 650 °C the relative amount of **8** decreases and phenylacetylene (**2a**) appears (Table II). At 760 °C the exclusive products are **1a** and **2a**.[12]



7 8

Such changes in product composition with increasing temperature can be interpreted[13] as a mechanistic change from a concerted process to a less concerted heterolytic or radical pair process at high temperature. Phenylacetylene (**2a**) and acetophenone (**1a**) are produced from a secondary pyrolysis reaction of first formed dione **8** at 750 °C (see Table II). A heterolytic or radical pair process may be operating.

Experimental Section

Thermal Dehydration of Acetophenone. Our apparatus consisted of a horizontal quartz reactor 1.5 cm in diameter and 40 cm long which was connected at one end to a 50-mL flask containing acetophenone and at the other end to a dry ice trap and vacuum source. The UOP No. 1 was supported in the quartz tube by either glass wool or steel wool. Steel or glass chips were mixed with the UOP No. 1 to improve the gas flow through the tube. We observed identical results with either glass or steel. A horizontal oven was used to vary the temperature which was measured by a thermocouple at the approximate center of the tube. The UOP No. 1, 5 g, was first heated to desired temperature, at which time water was driven off and then 5 g of acetophenone

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(2) (a) See also S. Kano, T. Yokomatsu, and S. Shibuya, *J. Org. Chem.*, **43**, 4366 (1978), and references cited therein. (b) P. A. Bartlett, F. R. Green III, and E. H. Rose, *J. Am. Chem. Soc.*, **100**, 4852 (1978), and references cited therein.

(3) D. E. van Horn and E. Negishi, *J. Am. Chem. Soc.*, **100**, 2252 (1978), and references cited therein.

(4) R. F. Kovan, G. F. L. Ehlers, and F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1081 (1977).

(5) See J. A. Mitchell and E. E. Reid, *J. Am. Chem. Soc.*, **53**, 330 (1931), for early work on the dehydrations of ketones.

(6) W. J. Bailey and F. Cesare, *J. Org. Chem.*, **43**, 1421 (1978).

(7) R. E. Smith and C. N. Hinshelwood, *Proc. R. Soc. London, Ser. A*, **176**, 468 (1940).

(8) UOP No. 1 is a commercial solid phosphoric acid polymerization catalyst formed by mixing together P_2O_5 and silica and then dehydrating at elevated temperatures. This material was obtained from Universal Oil Products.

(9) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(10) J. C. Craig and M. Moyle, *J. Chem. Soc.*, 3712 (1963).

(11) Similar results have also been reported F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3635 (1950).

(12) Acetic acid has also been observed.

(13) H. Kwart, T. J. George, R. Louw, and W. Ultee, *J. Am. Chem. Soc.*, **100**, 3927 (1978).

Table I. Pyrolysis of Acetophenone over UOP No. 1

reactant[a]	temp, °C	pressure,[b] mmHg	% 2a[f]
1a	400	0.4	2
1a	500	0.6	11
1a	630	0.7	28
1a	500	33	4
1a	582	760[e]	2
1a[c]	614	760[e]	3
1a[c]	600	0.5	21
1a[d]	600	0.5	0

[a] 5 g of acetophenone and 5 g of UOP No. 1 were used. [b] All of the acetophenone had passed through the tube in 30-60 min. This corresponds at 600 °C (1 mmHg) to a residence time of 0.3-0.6 s. [c] 20 g of UOP No. 1 was used. [d] Run without UOP No. 1 present. [e] 0.5 SCFM flow of N_2 was used. [f] Acetophenone (1a) and small amounts of water were also recovered. A mass greater than 90% was typically observed.

Table II. Pyrolysis of 7 at Various Temperatures[a]

reagent	temp, °C	pressure, mmHg	% 2a	% 1a	% 7	% 8
7	420	0.03			95	
7	534	0.03			92	tr
7[b]	529	0.05			95	tr
7	650	0.05	5	6	9	72
7	700	0.05	6	12	36	36
7	760	0.7	30	30		
8	760	0.4	37	60		
2a	700	0.2	95			

[a] Without catalyst, product collected in dry ice bath. [b] Contained large acidic glass surface area.

was placed in the reactor and allowed to flash distill through the tube. Reactions at atmospheric pressure were carried out under a nitrogen flow of 0.5 SCFM. Volatile products were collected in dry ice/acetone. Then the products were dissolved in ether and dried over anhydrous magnesium sulfate and the ether was removed in vacuo under conditions where losses of phenylacetylene or acetophenone were minimized. The products were analyzed by NMR and GC on a 2-ft UCW 982 column and by comparison with authentic samples. Results are shown in Table I.

Synthesis of Diethyl 1-Phenylvinyl Phosphate (5). To 15.5 g (0.1 mol) of phenacyl chloride in a 200-mL one-neck flask was added 16.6 g (0.1 mol) of triethyl phosphite. This was heated at 86 °C for 4 h with stirring. The product was then distilled at 121 °C (0.03 mm) [lit.[10] bp 101–105 °C (0.005 mm)], and 21.9 g was recovered: 86% yield; NMR ($CDCl_3$) δ 7.2–7.8 (m, 5 H, aromatic H), 5.25 (d, 2 H, $C{=}CH_2$, J = 3 Hz), 4.20 (q, 2 H, OCH_2, J = 8 Hz), 4.33 (q, 2 H, OCH_2, J = 8 Hz), 1.38 (t, 6 H, CH_3, J = 8 Hz).

Preparation of 1-Phenylvinyl Acetate (7). To 40 mL of isopropenyl acetate in a flask equipped with a magnetic stirrer and distillation head was added 24 g (0.2 mol) of acetophenone and 0.2 g of *p*-toluenesulfonic acid. After heating for 7 h at 98–118 °C, 15 mL of acetone had distilled and approximately 75% conversion to 7 was observed by NMR sampling of the product mixture. The reaction was then cooled, extracted with ether, and washed once with 10 g of sodium bicarbonate in 100 mL of ice water. The ether was then dried over anhydrous magnesium sulfate and removed in vacuo. The product distilled at 90 °C (4 mm)[lit. 92–95 °C (4.5 mm)][14] and 18 g was recovered: 56% yield; NMR ($CDCl_3$) δ 7.4 (m, 5 H, ring H's), 5.60 (d, 1 H, $C{=}CH$, J = 2 Hz), 5.10 (d, 1 H, $C{=}CH$, J_1 = 2 Hz), 2.30 (s, 3 H, CH_3).

Pyrolysis on 7 to Form 1-Phenyl-1,3-butanedione. Enol acetate (7; 2.0 g) was flash distilled through a quartz pyrolysis tube at 650 °C at 0.5 mm of vacuum. The product 8 (1.81 g, 90% yield) was collected in an ice bath and recrystallized from ethanol-water: mp 56–57 °C (lit.[11] mp 60 °C); NMR ($CDCl_3$) δ 7.2–8.0 (m, 5 H, ring H), 6.20 (s, 1 H, vinyl H), 2.60 (s, 2 H, CH_2 keto form), 2.20 (s, 3 H, CH_3). The product 8 was present in keto and enol forms and gave a positive ferric chloride test. Results for pyrolysis of 7 at other temperatures are reported in Table II. All products were identified by comparison with authentic samples (NMR, GC).

Registry No. 1a, 98-86-2; **2a**, 536-74-3; **5**, 1021-45-0; **6a**, 93-55-0; **6b**, 673-32-5; **7**, 2206-94-2; **8**, 93-91-4; phenacyl chloride, 532-27-4; triethyl phosphite, 122-52-1; isopropenyl acetate, 591-87-7.

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[14] D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.*, **91**, 119 (1969).

Convenient One-Step Synthesis of N-Substituted α-Methylphenethylamines via Aminomercuration–Demercuration

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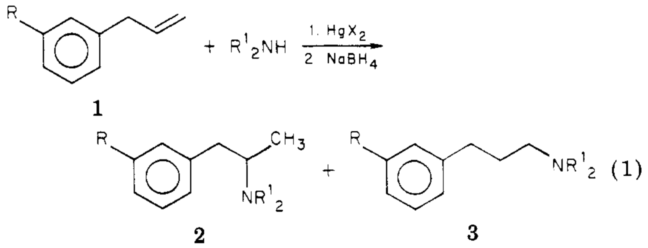
Phenethylamines are important natural precursors to a variety of alkaloid systems[1] as well as large ring benzoheterocycles[2] and are themselves also widely used as drugs.[3]

In our present work, we considered the recently developed[4] aminomercuration–demercuration reaction as a possible general route to N-substituted α-methylphenethylamines via a reaction of type 1, the Markownikoff product 2 being the desirable addend for our purposes. No such route to N-substituted amphetamines has been previously described. Of particular interest to us was the synthesis of the aminoacetaldehyde diethyl acetal derivative **2a** (R = OCH_3; R^1 = H, $CH_2CH(OEt)_2$), which is a useful synthon for the preparation of 3*H*-3-benzazepines.[5]



Our initial studies involved, as a prototype reaction, the addition of *m*-methoxyallylbenzene (1.2 equiv) to a mixture of the appropriate mercuric salt (1.5 equiv) and aminoacetaldehyde diethyl acetal (4 equiv) in THF with subsequent heating to 60 °C to expedite formation of the intermediate organomercurials. In all cases, rapid formation of amine–mercury complexes was observed prior to the addition of the olefin substrate. The rate of aminomercuration proved to be a sensitive function of the mercuric salt employed. The order of reactivity of the various mercury salts increased in the order $HgCl_2$ <

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(1) S. W. Pelletier, "Chemistry of the Alkaloids", Van Nostrand-Reinhold, New York, 1970.

(2) Georges Hazebroucq, "Access to 1*H*-Tetrahydro-2,3,4,5-benzazepine-3-ones", Ph.D. Thesis, University of Paris, in Annales De Chimie, Series 14, Vol. 1, 1966.

(3) C. D. Leake, "The Amphetamines: Their Actions and Uses", Charles C. Thomas Co., Springfield, Ill., 1958.

(4) (a) A. Lattes and J. J. Perie, *C. R. Hebd. Seances Acad. Sci.*, **262**, 1591 (1966); (b) A. Lattes and J. J. Perie, *Tetrahedron Lett.*, 5165 (1967); (c) A. Lattes and J. J. Perie, *ibid.*, 2289 (1969).

(5) J. Likforman and J. Gardent, *C. R. Hebd. Seances Acad. Sci.*, **268**, 2340 (1969).

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