Experimental Section[12]

4,4-Dimethyl-2-phenylpyrrolidine (2).—A solution of 13 g (59 mmoles) of 3,3-dimethyl-4-nitrobutyrophenone[5] in 100 ml of absolute ethanol was treated with hydrogen at 3 atm pressure and room temperature in the presence of 1 g of 10% palladium-charcoal. Slightly more than 2 equiv of hydrogen was taken up in 11 days. The catalyst was removed by filtration, the solvent evaporated under reduced pressure, and the residue was transferred with the aid of a little ethanol to a small distilling flask. After removal of the ethanol, the material (presumed to be the corresponding amino ketone) was heated to 200°, whereupon water was formed and was removed by distillation and the material became red and then almost black. After cooling, the material was distilled under reduced pressure and 6 g (59%) of a substance believed to be **5** was obtained as a pale yellow liquid, bp 123–128° (15 mm), $n^{25}\mathrm{D}$ 1.5408. The infrared spectrum showed sharp peaks at 5.81 and 6.18 μ. The nmr spectrum showed a singlet at 1.09, a triplet at 2.63 (J = 2 cps), a triplet at 3.69 (J = 2 cps), a multiplet at 7.3, and a multiplet at 7.75 ppm with area ratios of 6:2:2:3:2, respectively. Vapor phase chromatography on a cyanosilicone column (see below) at 150° gave a peak at 10.2 min retention time and indicated the material to be 97% pure.

To a stirred solution of 2 g (53 mmoles) of lithium aluminum hydride in 75 ml of dry diethyl ether was added, dropwise, 3.5 g (20 mmoles) of the above product. The mixture was refluxed for 2 hr, cooled, and then treated by the careful addition of 8 ml of saturated sodium carbonate solution. Filtration, evaporation of the solvent, and distillation of the residue under reduced pressure gave 3 g (86%) of **2** as a colorless oil, bp 111–115° (8 mm), $n^{24}\mathrm{D}$ 1.5188, which formed a picrate, mp 180–183° after recrystallization from ethanol. Vapor phase chromatography on a cyanosilicone column (see below) at 150° gave a single peak with a retention time of 6.9 min. The infrared spectrum was recorded. The nmr spectrum showed a six-proton singlet at 1.09 (4-methyls), a two-proton pair of doublets at 2.77 with J = 10 cps (5-methylene), a one-proton pair of doublets at 4.2 with J = 7 cps (2-methine), and a five-proton multiplet centered at 7.2 ppm (2-phenyl). The signals for the 3-methylene protons and the proton on the nitrogen consisted of a series of sharp lines centered at 1.6 ppm extending over a region of 1.2 ppm.

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.22; H, 9.82; N, 8.14.

N-Methyl-1-phenylpentylamine.—To a stirred solution of 1.2 g (10 mmoles) of benzylidenemethylamine in 25 ml of dry ether under dry nitrogen and cooled to 0° was added, dropwise, 5 ml (12 mmoles) of a 15% solution of *n*-butyllithium in hexane.[13] The mixture was stirred for 15 min and then poured into an excess of 5% sulfuric acid. After being washed two times with ether, the acidic extract was made strongly basic with 50% sodium hydroxide and the organic layer which formed was extracted into ether and dried over sodium sulfate. Evaporation of the ether and distillation of the residue *in vacuo* gave 1 g (57%) of a colorless oil, bp 71–72° (0.7 mm), $n^{25}\mathrm{D}$ 1.5005. The nmr spectrum showed a singlet at 2.16, a triplet centered at 3.34 (J = 7 cps), and a peak at 7.1 ppm corresponding to the N-methyl, methine, and phenyl protons, respectively.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80. Found: C, 81.23; H, 10.61.

Reaction of 1-Benzyl-3,3-dimethylazetidine (1) with *n*-Butyllithium in Ether.—To a solution of 3.5 g (20 mmoles) of **1** in 150 ml of refluxing diethyl ether under dry nitrogen was added 25 ml (60 mmoles) of *n*-butyllithium as a 15% solution in hexane.[13] The color of the mixture became lemon yellow. Aliquot portions (2 ml) were taken at various times, worked up as described below, and analyzed chromatographically on an Aerograph Model 600 (Hy-Fi) apparatus using a 1/8 in. × 5 ft column of 20% XF-1150 (cyanosilicone) on 60–80 mesh Chromosorb W at 145°. Composition *vs.* time data are given in Table I.

After 24 hr the solution was cooled and excess butyllithium was destroyed by the dropwise addition of water. Sulfuric acid (5%, 100 ml) was added and the mixture was then extracted twice with ether. An excess of 50% sodium hydroxide solution was added to the acidic extract and the organic layer which formed was taken up in ether and dried over sodium sulfate. After careful removal of the solvent by distillation, chromatogaphic analysis of a sample of the residual amines gave the composition indicated in the last line of Table I and the yield of mixed amines, bp 55–90° (0.3 mm), was 3.0 g which was collected as 1.5 g of **1**, bp 55–65°, and 1.5 g of **1** mixed with other products, bp 65–90°. From the latter was isolated by chromatography on a preparative (0.25 in. × 6 ft) cyanosilicone column *ca.* 0.35 g each of **2** and **3** plus 0.75 g of **1** and *ca.* 0.05 g of higher boiling amines. No polymeric material was formed. A sample of **1** subjected to the work-up and isolation procedures was recovered unchanged. The properties of **2** (chromatographic retention time, $n^{25}\mathrm{D}$ 1.5200, infrared, and nmr spectra) were identical with those of an authentic sample. The identity of **3**, $n^{25}\mathrm{D}$ 1.4837, was shown by its infrared and nmr spectra. The latter displayed a singlet at 0.85 (methyl hydrogens), a singlet at 2.1 (methylene bonded to nitrogen), a triplet at 3.4 with J = 7 cps (methine hydrogen), and a peak at 7.1 ppm (phenyl hydrogens) having the correct relative areas.

Anal. Calcd for $C_{16}H_{27}N$: C, 82.33; H, 11.66; N, 6.00. Found: C, 82.31; H, 11.52; N, 6.25.

Registry No.—**1**, 13509-71-2; **2**, 13509-72-3; **3**, 13509-73-4; **5**, 13509-74-5; N-methyl-1-phenylpentylamine, 13509-75-6.

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[12] Boiling points and melting points are uncorrected. The latter were taken on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60 analytical nmr spectrometer and, unless otherwise noted, with carbon tetrachloride as the solvent. Values are reported in parts per million (δ) relative to tetramethylsilane as the internal standard.

(13) Foote Mineral Co., Exton, Pa.

The Decarboxylation of Benzoylacetic Acids in Aqueous Sulfuric Acid[1]

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In conjunction with studies of the hydration of arylpropiolic acids,[3] we have had occasion to examine the decarboxylation rate for several substituted benzoylacetic acids in a wide range of sulfuric acid media. The rate of decarboxylation of acetoacetic acid is not sensitive to change from a polar to a nonpolar medium, as shown by the classical studies of Westheimer and Jones.[4] Even changing from water to benzene results in only a very modest change in the rate of decarboxylation.[5] These studies support the commonly accepted mechansim for the decarboxylation by way of a cyclic process. The decarboxylation of acetoacetic acid is also not subject to acid catalysis, as shown by the studies of Swain, *et al.*,[5] and the more extensive studies of Pedersen.[6] The rate of decarboxylation of acetoacetic acid falls by only a factor of four in changing from 2% sulfuric acid to 8 *M* sulfuric acid.

Our studies show that this is a general phenomenon. We have measured the rates of decarboxylation for *p*-anisoylacetic acid (**1**), *p*-toluoylacetic acid (**2**), benzoylacetic acid (**3**), and *m*-chlorobenzoylacetic acid (**4**) in from 25 to 75% sulfuric acid solution. Measure-

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ments were made by following the change in ultraviolet spectra. Additionally we have examined the reaction in deuteriosulfuric acid. Results are summarized in Table I.

TABLE I
DECARBOXYLATION OF AROYLACETIC ACIDS IN SULFURIC ACID AT 25.0°

Substituted acetic acid	% H_2SO_4	10^5k-CO_2, sec^{-1}
p-Anisoyl	23.62	2.9
	23.63	3.1
	25.62	3.20
	27.03	2.9
	27.12	2.8
	33.05	2.55
	33.33	2.4
	33.36	2.5
	36.05	2.38
	37.75	2.36
	48.61	1.45
	30.29[a]	2.2
	34.83[a]	2.00
	40.10[a]	1.64
	41.44[a]	1.54
	42.65[a]	1.31
	44.34[a]	1.36
p-Toluoyl	37.50	2.68
	42.00	2.2
	48.84	1.6
	52.72	1.4
	53.69	1.2
	61.37	0.732
	60.70[a]	0.730
Benzoyl	62.33	0.43
	67.40	0.406
	70.36	0.347
	65.85[a]	0.33
	66.68[a]	0.524
	68.64[a]	0.39
	71.71[a]	0.279
m-Chlorobenzoyl	74.38	0.230
	76.72	0.190
	78.11	0.170

[a] $ArCOCD_2CO_2D$ in D_2O-D_2SO_4; wt % D_2SO_4.

These results show that, in common with acetoacetic acid, the rates of decarboxylation of aroylacetic acids likewise are relatively insensitive to strong mineral acid concentration. The modest decrease in the rate of decarboxylation of anisoylacetic acid in changing from 25 to 48% sulfuric acid as the medium is very similar to the decrease observed by Pedersen with acetoacetic acid in sulfuric or perchloric acid solutions. Even in the higher concentrations of sulfuric acid, 60-70%, used with **3** and **4**, the observed behavior is similar.

Additionally, the reactivity of this group of compounds shows little sensitivity to the nature of the substituent in the aromatic moiety. Where the data are overlapping, **1** and **2** show very similar rates of decarboxylation; **3** and **4** appear to be slightly less reactive, but within a factor of 2. Swain, *et al.*,[5] concluded that ρ was about -1 in benzene solution for the decarboxylation of the aroylacetic acids.

In deuteriosulfuric acid, the decarboxylating species is the trideuterio analog. The decarboxylation of anisoylacetic acid in deuteriosulfuric acid shows only a very slightly depressed rate of reaction, which represents the combination of the factors discussed previously by Swain, *et al.*,[5] which are involved in the proton-transfer process concomitant with the decarboxylation; our system also includes secondary isotope effects from the CD_2 moiety, as bonding changes from tetrahedral to trigonal. In the case of **1**, the isotope effect is normal, though small. Swain found similar values for **1** and **3** but a slightly inverse value (k_H/k_D = 0.85) for **2** in benzene solution.[5]

Experimental Section

Materials.—***p*-Anisoylacetic acid** (1) was prepared following the procedure of Swain, *et al.*,[5] mp 80-81° dec (lit.[5] mp 80°, 81-82° dec). ***p*-Toluoylacetic acid** (2) was prepared by saponification of ethyl *p*-toluoylacetate. On purification by reprecipitation from carbonate solution and drying, **2** was obtained, mp 87-88° dec (lit.[5] 85-87° dec). A small sample was further purified to mp 89.7-90.2° dec.

Kinetic Procedures. A.—The appropriate β-keto acid was *dissolved in 95% sulfuric acid, and a small volume of this solution* was added to more dilute sulfuric acid to make a solution of the desired concentration (5×10^{-5} *M*) in sulfuric acid of the appropriate concentration. Measurements were made using a Beckmann DU spectrophotometer at an appropriate wavelength (260-280 mμ). Stock solutions of **1** and **2** were reasonably stable in 95% acid for 2 weeks.

B.—The β-keto acid was generated *in situ* by the hydration of the appropriate arylpropiolic acid.[8] The conversion of the β-keto acid into the acetophenone was followed spectrophotometrically.

Registry No.—**1,** 13422-77-0; **2,** 13422-78-1; benzoylacetic acid, 614-20-0; *m*-chlorobenzoylacetic acid, 13422-80-5; sulfuric acid, 7664-93-9.

Photochemical Reaction of 1,3,4,6-Tetraphenylhexa-1,3,5-triene[1]

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Theis and Dessy have reported that 1,3,4,6-tetraphenyl-1,3,5-hexatriene (1) upon irradiation with light of wavelengths above 280 mμ gave one photoproduct which could be isolated in 87% yield.[3] The photoproduct was postulated to be 1,2,3,5-tetraphenyl-1,4-cyclohexadiene (2).[3] This result is contrary to the previous results in the photochemistry of conjugated cyclohexadienes[4] and, in particular, of phenyl-substituted cyclohexadienes.[5] In these cases, the first formed photoproduct is either a hexatriene[4,5] or a bicyclo[2.2.0]hexene.[6] When the examples which form

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[2] NASA Predoctoral Trainee, 1964-1967.

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