mately 8 by $NaHCO_3$ addition. The insoluble product was washed with water, ether, and absolute alcohol and dried to give 1.4 g (81% yield), mp 187° dec.

Anal. Calcd for $C_6H_4I_2O$: C, 20.83; H, 1.17; mol wt (iodometric), 346. Found: C, 20.94; H, 1.25; mol wt, 352.

1,3-Diacetoxy-1,3-dihydro-1,3,2-benzodiiodoxole (V).—*o*-Diiodobenzene (1 ml, 2.5 g) was dissolved in 5 ml of glacial acetic acid, warmed to 30°, and treated with 5 ml of 40% peracetic acid, dropwise and with good stirring. After all the peracetic acid had been added, the mixture was stirred for another 20 min; 100 ml of water was then added to yield a thick white crystalline precipitate. The precipitate was filtered and washed with ether, recrystallized from 4 *N* acetic acid, and dried to yield a fine, glass woollike product (0.9 g, 0.26%), mp 226–229°.

Anal. Calcd for $C_{10}H_{10}I_2O_5$: C, 25.86; H, 2.16; mol wt, 464. Found: C, 25.21, 25.25; H, 2.39, 1.98; mol wt (iodometric), 460.8.

1-Acetoxy-3-hydroxy-1,3-dihydro-1,3,2-benzodiiodoxole (VII).—1,3-Diacetoxy-1,3-dihydro-1,3,2-benzodiiodoxole (1 g) was triturated with distilled water to yield a fine yellow granular powder, washed with water, and dried to give 0.9 g, mp 214°.

Anal. Calcd for $C_8H_8I_2O_4$: C, 22.74; H, 1.89; mol wt, 422. Found: C, 23.20; H, 1.88; mol wt, 418.5.

1,3-Dichloro-1,3-dihydro-1,3,2-benzodiiodoxole (IX).—1-Acetoxy-3-hydroxy-1,3-dihydro-1,3,2-benzodiiodoxole (1 g) was suspended in 300 cc of 1 *N* NaOH and stirred until all the yellow powder was completely dissolved. The mixture was stirred for several hours and showed a clear yellow-green color. Slow addition of concentrated HCl resulted in the precipitation of a fluocculent light yellow powder. The product was recrystallized from dilute base: yield, 0.8 g (80%); mp 167–170°.

Anal. Calcd for $C_6H_4Cl_2I_2O$: C, 17.26; H, 0.96; I, 60.9; Cl, 17.39; O, 3.89; mol wt, 417. Found: C, 17.81, 17.73; H, 1.00, 1.10; I, 60.2; Cl, 17.02, 16.52; O, 4.76; mol wt, (iodometric) 415.6.

Registry No.—II, 13509-76-7; IV, 13509-77-8; V, 13509-78-9; VII, 13509-79-0; IX, 13509-80-3.

Azetidines. I. The Wittig Rearrangement of a 1-Benzylazetidine[1,2]

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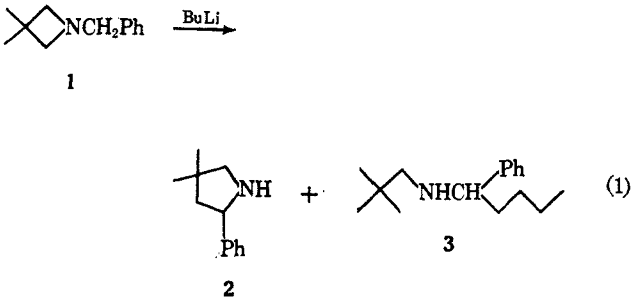
In the course of an investigation of the butyllithium-induced rearrangement of 1,1-dibenzyl-3,3-dimethylazetidinium bromide,[3] it was found that appreciable amounts of 1-benzyl-3,3-dimethylazetidine (1) and *n*-pentylbenzene were formed (in addition to rearrangement products) in a nearly equimolar ratio. The yield of 1 was 13% when the reaction was carried out at −2°. When the reaction temperature was 36°, however, the yield of 1 was only 0.7% and three new amines were formed in yields of 4.3, 5.6, and 0.4%. Further examination of this latter aspect of the reaction revealed what is believed to be the first example of a 1,2-rearrangement of a tertiary benzylamine to a secondary amine.

Treatment of an ethereal solution of 1 with a 3 *M* excess of butyllithium at reflux temperature afforded 4,4-dimethyl-2-phenylpyrrolidine (2) (*ca.* 19%) and N-(2′,2′-dimethylpropyl)-1-phenylpentylamine (3) (*ca.* 17% (eq 1). The remaining material was the starting compound (1) and a small quantity (*ca.* 2%) of higher boiling amines.[4] The temporal course of the reaction was followed by the vapor phase chromatographic analysis of aliquots at intervals (Table I). It was noted that the reaction slowed down markedly after a few hours and had essentially stopped after 24 hr even though about 65% of the starting material could still be recovered.



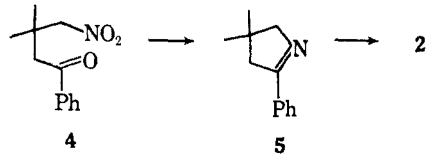
(1)

Table I

Data on Reaction of 1 with Butyllithium in Ether

Time, hr	Product compn, mole % 1	2	3
0.5	92.1	2.2	5.7
2.5	77.0	8.6	14.4
3.5	73.9	10.1	16.0
10.5	66.3	17.9	15.8
24	64.7	18.6	16.7

The structure of 2 was established by its absorption spectra (infrared and nmr) and analysis and confirmed by comparison with the product from the lithium aluminum hydride reduction of 4,4-dimethyl-2-phenyl-1-pyrroline (5) which was in turn prepared by reduction and cyclization of the known[5] 3,3-dimethyl-4-nitrobutyrophenone (4) (eq 2). The structure of the ring-opened product (3) was revealed by the nmr spectrum and by comparison of this with that of a model compound, N-methyl-1-phenylpentylamine, readily prepared by the reaction of benzylidenemethylamine and butyllithium.



(2)

These results are remarkable in two respects. First, although the Wittig rearrangement[6] has been studied extensively,[7,8] the reaction has heretofore been observed only with ethers (with which good results are obtained

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[1] From the Ph.D. Thesis of Max T. Wills, University of Washington.

[2] Supported in part by State of Washington Initiative 171 Funds for Research in Biology and Medicine. Preliminary report: A. G. Anderson and M. T. Wills, *Angew. Chem.*, **79**, 574 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 557 (1967).

[3] Further results from the study of this and other reactions of strong bases on quaternary azetidinium salts will be reported in succeeding publications in this series.

[4] An attempt to effect this reaction with the weaker base phenyllithium gave only recovered starting material.

[5] L. I. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **71**, 2671 (1949).

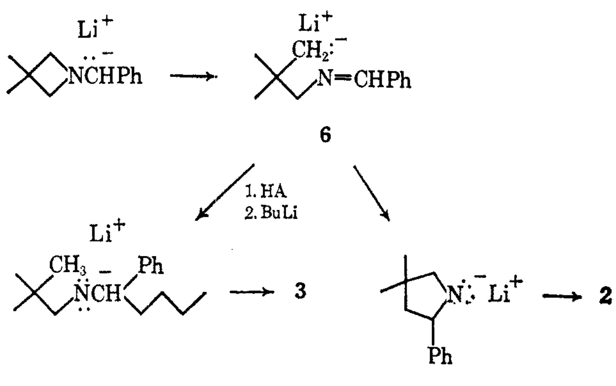
[6] G. Wittig and L. Löhmann, *Ann.*, **550**, 260 (1942).

[7] For leading references, see (a) H. E. Zimmerman, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 372–377; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 165, 230–233.

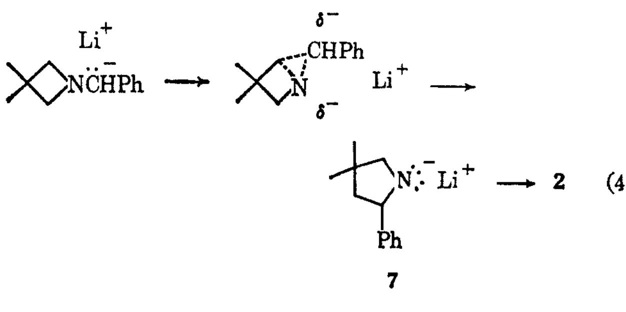
[8] For more recent studies of the Wittig rearrangement with particular reference to the mechanism, see (a) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, **88**, 78 (1966); (b) U. Schöllkopf and H. Schäfer, *Ann.*, **663**, 22 (1963); (c) Y. Makisumi and S. Notzumoto, *Tetrahedron Letters*, No. 51, 6393 (1966).

only when a hydrogen α to the oxygen is also adjacent to a conjugated system). Second, Hauser and co-workers[9] have examined the metalation of several tertiary benzylamines with butyllithium and report that *ortho* metalation is the exclusive reaction with benzyldimethylamine. These authors obtained evidence that the *ortho* metalation occurred directly in this case and that α metalation was not involved. In the present case, the formation of rearrangement products indicates the existence of an α-lithio intermediate. The consumption of about 65% of the starting amine such that it does not rearrange but is completely recoverable points to the eventual formation of the *o*-lithio derivative to this extent. The results do not reveal how much of the α-lithio species originally formed was "lost" by isomerization to the (presumably *o*-lithio) structure which did not rearrange, but show that a minimum of 35% of α-metalated amine was formed.

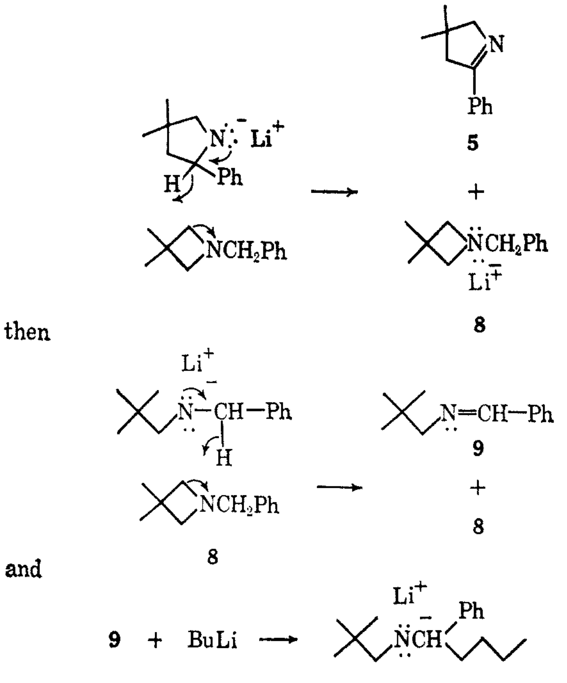
It was of interest to see if this amine rearrangement could be interpreted by ion pair (eq 3), SN1 (eq 4), and radical mechanisms analogous to those which have been proposed for the rearrangement of ethers.[7,8] A considerable amount of the driving force for the opening of the azetidine ring can be attributed to the relief of the strain in the four-membered ring in each case. In eq 3 the order of the sequence of reactions of the ring-opened ion pair (6) with a proton source (*e.g.*, unreacted amine or solvent) and butyllithium would not alter the results, but the formation of a neutral intermediate (rather than a double charged anion) might be expected in the rather nonpolar medium. In eq 4 the rearrangement process leads directly only to the ring-enlarged product; an additional reaction of 7 is necessary to account for the incorporation of the butyl group in the acyclic product (see eq 5 below). This is an appreciably more complex scheme and would be therefore less attractive if it did not also provide a possible explanation for the formation of corresponding acyclic products in which two *n*-butyl groups have been introduced.[10] Support for the hypothesis of the hydride-transfer steps is provided by the demonstrated effectiveness of lithium diethylamide as a hydride donor.[11] An alternative possibility is that **7** could undergo ring opening by cleavage of a carbon–carbon bond to form **6** (eq 8), which would lead to **3** as indicated in eq 3.



(3)



(4)



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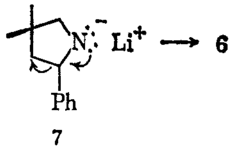
(6)

(7)



(8)

More recently, Lansbury, *et al.*,[8a] have suggested that the mechanism of the Wittig rearrangement involves cleavage–recombination with free-radical pairs as the intermediate species. The formulation of this type of mechanism to accommodate the present results appeared to involve features (*e.g.*, the formation of atomic lithium, or intramolecular hydrogen abstraction followed by reaction with butyllithium to form a dianion or by proton abstraction by the nitrogen prior to the alkylation step) which made it less attractive than eq 3 or 4. Further studies on the scope and mechanism of this new rearrangement are contemplated.

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[9] F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 701 (1962); F. N. Jones, M. F. Zinn, and C. R. Hauser, *ibid.*, **28**, 663 (1963); F. N. Jones, R. L. Vaulx, and C. R. Hauser, *ibid.*, **28**, 3461 (1963); W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 2467 (1963).

[10] Preliminary results of further studies indicate that the amines $(CH_3)_3CCH(n\text{-}C_4H_9)NHCH(n\text{-}C_4H_9)C_6H_5$ and $(CH_3)_3CCH_2NHC(n\text{-}C_4H_9)_2\text{-}C_6H_5$ are formed in very small amounts when the reaction is carried out in ether and in larger amounts (13% total) when the reaction is carried out in hexane.

[11] G. Wittig and H. D. Frommeld, *Ber.*, **97**, 3541, 3548 (1964).

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}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}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}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}D 1.5200, infrared, and nmr spectra) were identical with those of an authentic sample. The identity of **3**, n^{25}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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[1] Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

[2] National Science Foundation Predoctoral Fellow, 1962–1965.

[3] D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Am. Chem. Soc.*, **87**, 2295 (1965).

[4] F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).

[5] C. G. Swain, R. F. W. Bader, R. M. Esteve, Jr., and R. N. Griffin, *J. Am. Chem. Soc.*, **83**, 1951 (1961).

[6] K. J. Pedersen, *Acta Chem. Scand.*, **15**, 1718 (1961).