one equivalent of hydrogen was absorbed. The catalyst was removed by filtration and washed with acetone. The acetone was removed by evaporation and the acetic acid solution was added to about 200 ml. of water. The mixture was chilled and filtered to provide 5.0 g. (83%) of colorless 5-methyl-2,3,5,6-tetrahydrofuro(3,2-g)coumarin, m. p. 62–65°. Recrystallization from ether–cyclohexane gave an analytical sample melting at 68.5–69.5°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.93. Found: C, 70.42; H, 5.73.

Summary

A study of the dehydrogenation of a number of 2,3-dihydrofurocoumarins to the corresponding furocoumarins is described.

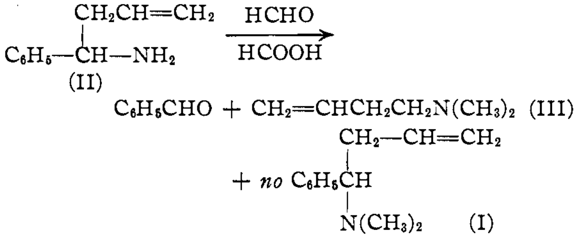
PHILADELPHIA 4, PENNA. RECEIVED JULY 28, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

A Cleavage Reaction of α-Allylbenzylamines

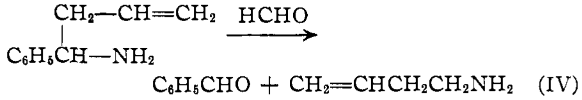
BY ROBERT M. HOROWITZ AND T. A. GEISSMAN

In an attempt to prepare α-allylbenzyldimethylamine (I), α-allylbenzylamine (II) was treated with formic acid and formaldehyde under the conditions described by Clarke, Gillespie and Weisshaus.[1] Instead of the methylation of II to I, the reaction took a different course, leading to cleavage of II with the formation of benzaldehyde and 1-dimethylaminobutene-3 (III)



$$\underset{\text{(II)}}{C_6H_5{-}\overset{\overset{\displaystyle CH_2CH{=}CH_2}{|}}{C}H{-}NH_2} \xrightarrow[\text{HCOOH}]{\text{HCHO}} C_6H_5CHO + CH_2{=}CHCH_2CH_2N(CH_3)_2 \text{ (III)} + \textit{no}\ C_6H_5\overset{\overset{\displaystyle CH_2{-}CH{=}CH_2}{|}}{\underset{\underset{\displaystyle N(CH_3)_2}{|}}{C}}H \text{ (I)}$$

Examination of this reaction disclosed that the cleavage was brought about by the action of formaldehyde on II, III being formed by the subsequent methylation of the 1-aminobutene-3 (IV) produced in the initial phase of the reaction. This was demonstrated by carrying out the reaction in the absence of formic acid. The products were benzaldehyde and IV

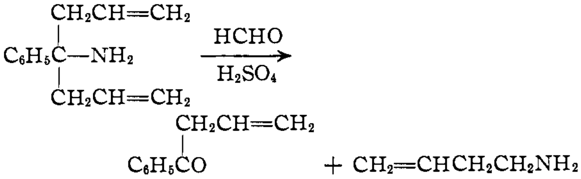


$$C_6H_5\overset{\overset{\displaystyle CH_2{-}CH{=}CH_2}{|}}{C}H{-}NH_2 \xrightarrow{\text{HCHO}} C_6H_5CHO + CH_2{=}CHCH_2CH_2NH_2 \text{ (IV)}$$

The structure of the butenylamine was demonstrated by its reduction to *n*-butylamine, identified by means of the picrate. 1-Dimethylaminobutene-3 was identified by comparing its picrate and methiodide with those of an authentic sample prepared by the method of Robinson and Robinson[2] who prepared the diethylamino analog by the reaction of allylmagnesium chloride with butoxymethyldiethylamine. The use of butoxymethyldimethylamine led to III.

In view of this unusual result, it was of importance to prove conclusively that the starting compound (II) was indeed α-allylbenzylamine, and that the cleavage of the carbon chain had not occurred at some earlier stage. α-Allylbenzylamine was prepared in excellent yield by the Hofmann degradation of α-allylphenylacetamide. That the product of this reaction was indeed II was shown by the preparation of an alkali-soluble benzenesulfonamide, a 3-nitrophthalimide, and a trimethylammonium iodide. The latter upon Hofmann degradation afforded 1-phenylbutadiene, identified by the preparation of its dibromide.

The reaction of formaldehyde with α,α-diallylbenzylamine was also examined, and it was found that cleavage occurred in the same manner as before, leading to 1-aminobutene-3 and a ketone, presumably allyl phenyl ketone. The characterization of the ketone by means of its 2,4-dinitrophenylhydrazone yielded a product which did not show a sharp melting point until it had been recrystallized repeatedly. The final product showed the correct analysis for allyl-(or propenyl) phenyl ketone. It seems likely that the melting point range of the derivative is explainable by a partial isomerization of the double bond either in the reaction in which the ketone was formed or in the preparation of the dinitrophenylhydrazone. The point was not of importance to the cleavage reaction, however, since hydrogenation of the unsaturated ketone yielded *n*-butyrophenone, thus establishing the fact that the cleavage reaction proceeded as shown



$$C_6H_5\overset{\overset{\displaystyle CH_2CH{=}CH_2}{|}}{\underset{\underset{\displaystyle CH_2CH{=}CH_2}{|}}{C}}{-}NH_2 \xrightarrow[H_2SO_4]{\text{HCHO}} C_6H_5\overset{\overset{\displaystyle CH_2CH{=}CH_2}{|}}{C}O + CH_2{=}CHCH_2CH_2NH_2$$

α,α-Diallylbenzylamine was prepared by the action of excess allylmagnesium bromide on benzonitrile, a reaction analogous to many investigated by Henze and his collaborators.[3] Its structure is established by the method used for its synthesis. It was characterized by the preparation of its benzenesulfonamide and the thiourea formed by the action of phenyl isothiocyanate. The course of the cleavage reaction can be formulated as

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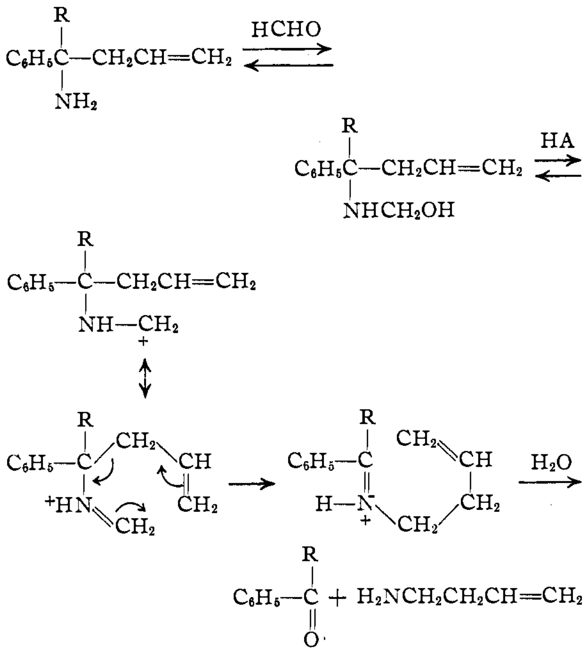
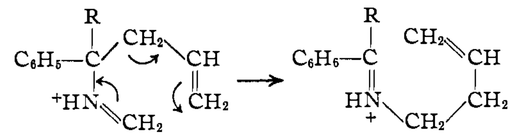
[1] Clarke, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[2] Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

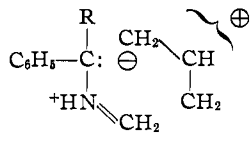
[3] Henze, Allen and Leslie, THIS JOURNAL, **65**, 87 (1943).



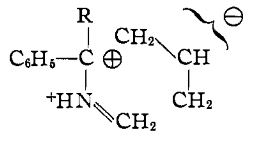
The evidence is not yet sufficient to enable a choice to be made between the rearrangement of bonds as shown above and that shown in the alternative scheme



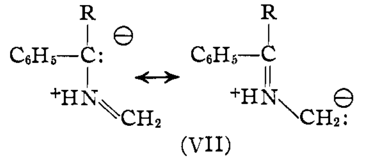
The first of these alternatives is suggested, however, since for it can be visualized the transition state V, while for the latter the transition state VI would be written. Since the nitrogen-containing moiety in V can be stabilized by the resonance VII while in VI this fragment must be written with two adjacent positive charges, the course through V seems the more likely. Experiments to test this assumption are in progress.



V

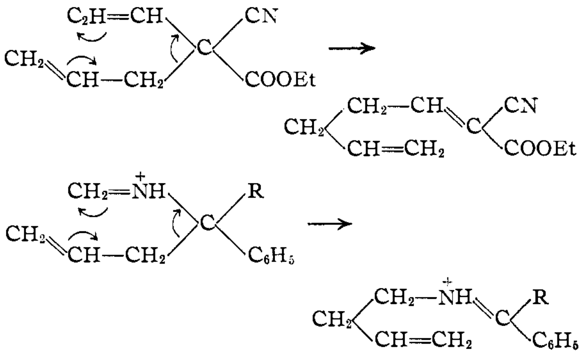


VI



(VII)

This cleavage reaction, while unique, appears to bear a formal resemblance to the rearrangement of allylvinylmalonic acid derivatives described by Cope.[4,5] The rearrangement of allylvinylcyanoacetic ester and of the conjugate acid of the methylol derivative of α-allylbenzylamine are written below in such a way as to show this resemblance



Although the rearrangement of the allylbenzylamines is written as proceeding through a cyclic intermediate (transition) state, with consequent inversion of the allyl group, this remains to be substantiated by experiments in which α- or γ-substituted allyl groups are used. Such experiments will be described in forthcoming papers.

Experimental

α-Allylphenylacetic Acid.—This was prepared in 73% yield by the rearrangement allyl phenylacetate by means of sodium hydride.[6]

α-Allylphenylacetamide.—A solution of 57.0 g. (0.478 mole) of thionyl chloride in 50 ml. of dry ether was added gradually to a mixture of 84.4 g. (0.478 mole) of α-allylphenylacetic acid, 37.8 g. (0.478 mole) of dry pyridine and 250 ml. of dry ether. The mixture was stirred for several hours and allowed to stand overnight. The liquid was separated by decantation and the solvent removed under reduced pressure. The residual acid chloride was added dropwise with stirring to 500 ml. of ice-cold concentrated aqueous ammonia. The solid which separated was collected, dried and recrystallized from benzene–ligroin. The weight of pure amide, m. p. 53.5–54°, was 69 g. (82%).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.33; H, 8.00.

α-Allylbenzylamine.—A solution of sodium hypobromite was prepared by the successive addition of 100 g. (2.5 moles) of sodium hydroxide and 80.7 g. (0.505 mole) of bromine to 750 ml. of ice-water. All but 35 ml. of the cold hypobromite solution was added dropwise with ice-cooling during one and one-half hours to a rapidly stirred suspension of 68.0 g. (0.388 mole) of powdered α-allylphenylacetamide in 300 ml. of water. After the addition of the hypobromite, the solution was filtered with the aid of suction to remove a trace (about 0.5 g.) of unreacted amide. (Note: it is advantageous to stop the addition of the hypobromite when it begins to react more slowly—as shown by the rate of disappearance of the yellow color—even though some unreacted amide is still present.) The filtered solution was warmed at 70° for two hours, cooled and extracted with ether. The ether solution was dried over anhydrous potassium carbonate and distilled through

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(4) Cope, *et al.*, THIS JOURNAL, **62**, 441 (1940); **63**, 1843, 1852 (1941); **65**, 1999 (1943); **64**, 1684 (1944).

(5) Although the reaction of the allylbenzylamines is called a cleavage, it is evident that the fundamental change is a rearrangement, the product of which is a Schiff base. The hydrolysis of this unstable intermediate constitutes the actual cleavage reaction.

(6) Arnold and Searles, THIS JOURNAL, **71**, 1150 (1949).

a short column. α-Allylbenzylamine distilled at 75° at 3.5 mm.; it was a mobile, colorless liquid having a strongly ammoniacal odor. In two experiments the yields of amine were 89 and 90%; $d^{24}{}_4$ 0.953; $n^{20}{}_D$ 1.5300; M_D (calcd.) 47.85, M_D (found) 47.8.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.59; H, 8.90; neut. equiv., 147.2. Found: C, 81.83; H, 9.03; neut. equiv. (in alcohol, to methyl red end-point), 146.8.

N-(α-Allylbenzyl)-benzenesulfonamide.—The reaction of α-allylbenzylamine with the calculated amount of benzenesulfonyl chloride in dilute, aqueous sodium hydroxide led to the formation of the sodium salt of the amide, which crystallized from the solution in fine needles and dissolved upon dilution with water. Acidification of the clear solution precipitated the amide, which was recrystallized from 50% ethanol as long, slender needles, m. p. 79.5–80.5°.

Anal. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; N, 5.96. Found: C, 66.97; N, 6.19.

N-(α-Allylbenzyl)-3-nitrophthalimide.—A mixture of 0.5 ml. of α-allylbenzylamine and 1.3 g. of 3-nitrophthalic anhydride was heated to 170° for five minutes, cooled and triturated with sodium bicarbonate solution. The residual solid was recrystallized from alcohol. It formed shining plates, m. p. 98–99°.

Anal. Calcd. for $C_{18}H_{24}N_2O_4$: C, 67.07; H, 4.38. Found: C, 67.01; H, 4.59.

α-Allylbenzylamine Picrate.—The addition of 1.0 g. of the amine to a solution of 1.4 g. of picric acid in ether resulted in the immediate formation of a mass of yellow needles. Recrystallized from alcohol, the picrate melted at 153°.

Anal. Calcd. for $C_{16}H_{16}N_4O_7$: C, 51.06; H, 4.29. Found: C, 51.01; H, 4.40.

When an attempt was made to recrystallize the picrate from acetone, a new compound, crystallizing in yellow prisms, was formed; it had m. p. 149–151° and depressed the melting point of the picrate, m. p. 153°. It could be recrystallized from methanol, but it tended to revert to the original picrate in 95% ethanol. The compound appears to be **N-isopropylidene-α-allylbenzylamine picrate.**

Anal. Calcd. for $C_{19}H_{20}N_4O_7$: C, 54.80; H, 4.84. Found: C, 54.18; H, 4.92.

N,N,N-Trimethyl-N-α-allylbenzylammonium Methosulfate.—To a boiling slurry containing 10.0 g. (0.068 mole) of α-allylbenzylamine, 22.8 g. (0.272 mole) of sodium bicarbonate, 100 ml. of water and 100 ml. of ethanol was added 17.1 g. (0.136 mole) of dimethyl sulfate during twenty minutes. The mixture was boiled for two hours, cooled and treated with solid sodium hydroxide until two liquid phases appeared. The lower layer was extracted with ether and the extract combined with the upper layer. Evaporation of the ether left an oily residue from which a solid separated upon the addition of a few ml. of dry ether. After recrystallization of the solid from acetone it formed shiny platelets, m. p. 137–138°. It was water-soluble and left a residue when heated gently on a spatula.

Anal. Calcd. for $C_{14}H_{23}NSO_4$: C, 55.79; H, 7.69. Found: C, 55.78, 56.12; H, 8.31, 8.03.

Hofmann Degradation of Trimethyl-α-allylbenzylammonium Methosulfate: 1-Phenyl-1,3-butadiene.—A solution of 0.5 g. of the quaternary salt was added to 20 ml. of 1.5 *N* sodium hydroxide and the solution distilled until about 5 ml. of distillate had been collected. The upper layer of the distillate was separated with the aid of ether and the ether solution dried over anhydrous potassium carbonate and divided into two portions.

One portion was brominated at 0°, with the immediate formation of an unsaturated, powdery yellow solid, m. p. about 76°. Slow evaporation of the ether gave a different solid, m. p. 89.5–90° after repeated recrystallization from ligroin. Riiber[7] reports the melting point of the dibromide of 1-phenyl-1,3-butadiene as 94°. In view of this discrepancy the product was analyzed.

*Anal.**[7a] Calcd. for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48; Br, 55.11. Found: C, 41.63; H, 3.77; Br, 55.11.

The second portion of the original ether solution was treated with maleic anhydride and set aside overnight. Evaporation of the ether and recrystallization of the residual solid from ligroin yielded a white, bicarbonate-insoluble solid, m. p. 120.5–120.7°. The recorded melting point[8] of the adduct of maleic anhydride and 1-phenylbutadiene is 120°.

The Reaction of α-Allylbenzylamine with Formaldehyde in the Presence of Formic Acid.—(a) A mixture of 9.0 g. (0.30 mole) of trioxymethylene, 35 g. (0.68 mole) of 90% formic acid and 17 ml. of water was heated on the steam-bath until it became homogeneous. To the cooled solution was then added 20.0 g. (0.136 mole) of α-allylbenzylamine. The solution became yellow and the temperature rose to about 40° during thirty minutes. After being heated on the steam-bath for two hours the solution was set aside overnight. The addition of 15.7 g. of concentrated hydrochloric acid caused the appearance of two phases. Steam distillation of the mixture gave a two-phase distillate, the organic portion of which was taken up in ether. The ether solution was washed with sodium bicarbonate solution, dried and distilled. There was obtained 10.1 g. (70%) of benzaldehyde, b. p. 174°, identified by means of the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 237.5°.

(b) The following ingredients were treated as in part (a): 3.1 g. of trioxymethylene, 9.0 g. of 90% formic acid, 5 ml. of water and 5.0 g. of α-allylbenzylamine. The steam distillate, consisting of two phases and smelling strongly of benzaldehyde, was discarded. The residue from the steam distillation was made alkaline with sodium hydroxide and then steam distilled into a 25-ml. portion and a 200-ml. portion. The latter contained only about 10% of the titratable basicity. To the 25-ml. portion was added solid potassium hydroxide; an amine layer separated. This was removed with ether, the ether solution dried and added to an ether solution of 0.45 g. of picric acid. After several hours at 0°, a crystalline picrate separated, m. p. 103–105°. Several recrystallizations from alcohol raised the melting point to 110.2–111°. A mixed melting point with an authentic sample (see below) of the picrate of 4-dimethylaminobutene-1 showed no depression.

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 43.90; H, 4.91. Found: C, 44.11, 43.96; H, 5.11, 5.09.

A 0.2-g. sample of the picrate was steam distilled from a basic solution, the distillate extracted with ether and the ether solution dried over anhydrous potassium carbonate. The addition of methyl iodide to the solution resulted in the formation of the crystalline methiodide, m. p. 240–241.5° after recrystallization from chloroform–methanol. A mixed melting point with an authentic sample showed no depression. Examination of the mother liquors left from the original preparation of the dimethylbutenylamine picrate revealed the presence of a very small amount (30 mg.) of another picrate, m. p. 180–187°. This was not examined further.

(c) In a third experiment, 7.0 g. of α-allylbenzylamine, 15.5 g. of 36–38% formalin solution and 12.2 g. of 90% formic acid were combined. The odor of benzaldehyde became apparent immediately. When heat was applied to the solution an exothermic reaction took place with the evolution of carbon dioxide (collected in barium hydroxide solution).

In this experiment the yield of pure benzaldehyde isolated by distillation was 4.02 g. (80%). The amine was collected in three portions by steam distillation: (1) 25.8, (2) 25.8 and (3) 26.0 ml. containing, respectively, 6, 1.3 and 0.7 milliequivalents of base (12.6, 2.7 and 1.5%). From fraction 1 was isolated 0.9 g. of picrate, m. p. crude 97–99°, raised to 110° by recrystallization. The isolable

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[7] Riiber, *Ber.*, **36**, 1404 (1903).

[7a] Analyses marked by an asterisk were carried out by the Clark Microanalytical Laboratory, Urbana, Illinois.

[8] Diels and Alder, *Ber.*, **62B**, 2081 (1929).

yield of dimethylaminobutene is thus about 10%. From fractions 2 and 3 small amounts of impure picrates melting at around 170° were obtained. The residual undistilled solution contained higher amines, present in small amounts not yet investigated.

The Reaction of α-Allylbenzylamine with Formaldehyde in the Absence of Formic Acid.—A mixture of 2.44 g. (0.0166 mole) of α-allylbenzylamine, 3.0 ml. of 36–38% formalin solution and 20 ml. of water was heated in a pressure flask on the steam-bath for 3.5 hours, then cooled, acidified and extracted with ether. The ether extract yielded about 0.5 g. of benzaldehyde. The acidic aqueous layer was made alkaline and extracted with ether. From the ether extract was prepared a picrate, but this was impure and could not be recrystallized. The crude picrate was steam distilled from an alkaline solution. The distillate contained an unsaturated amine and afforded a picrate which, after recrystallization from *n*-butanol, formed needles, m. p. 136.8–137.4°. The analytical data were in accord with those expected for the picrate of 1-aminobutene-3.

*Anal.** Calcd. for $C_{10}H_{12}N_4O_7$: C, 40.00; H, 4.03; N, 18.66. Found: C, 39.98; H, 4.36; N, 18.96.

Several attempts to relate the primary amine to its N,N-dimethyl derivative by methylation were unsuccessful. The structure was proved by reduction to the known *n*-butylamine, as described in experiment (b).

(b) A mixture of 7.0 g. of α-allylbenzylamine, 7.74 g. of 36–38% formalin and 20 ml. of methanol was refluxed for ten hours. After the addition of 15 ml. of 6 *N* sulfuric acid, steam distillation afforded 4.06 g. (81%) of benzaldehyde, b. p. 174° (uncor.).

The residual solution was made alkaline and steam distilled. The first 25 ml. (a) of distillate contained 0.0232 equivalent of base (48%), a further 0.0038 equivalent (8%) being contained in the second portion (b) of 70 ml. A part of fraction (a) was used for the preparation of the picrate, m. p. 137.5–137.9°. A 3.5-ml. portion of fraction (a) was added to 50 ml. of absolute ethanol containing 100 mg. of prereduced platinum oxide. The mixture was shaken with hydrogen until no more was absorbed. The solution was acidified, evaporated, made basic and steam distilled. The addition of picric acid to the distillate resulted in the formation of a picrate, m. p. 144–144.5°. This proved to be identical with an authentic sample of the picrate of *n*-butylamine, m. p. mixed m. p. 144–144.5°. From fraction (b) was isolated a very small amount of an impure picrate melting unsharply at about 90°.

Treatment of α-Allylbenzylamine with Acid.—After the treatment of 2 g. of α-allylbenzylamine with 200 ml. of boiling 6 *N* sulfuric acid, no amine other than the starting material was present, as shown by the preparation of the picrate.

1-Dimethylaminobutene-3.—A slurry of 62 g. (about 0.75 mole) of 36–38% formalin, 193 ml. (0.85 mole) of "technical" aqueous dimethylamine, 58 g. (0.785 mole) of *n*-butanol and an excess of anhydrous potassium carbonate was allowed to stand overnight. The organic layer was taken up in ether and distilled. Butoxymethyldimethylamine (not further purified) distilled at 138–138.5°. This was treated with an excess of allylmagnesium bromide, each drop of the reagent causing the formation of a white precipitate. The ether layer was separated and extracted with dilute hydrochloric acid. The desired amine was separated by steam distillation, followed by distillation through a Vigreux column. The amine boiled at 92°.[9]

Anal. Calcd. for $C_6H_{13}N$: C, 72.66; H, 13.21; N, 14.13; neut. equiv., 99.2. Found: C, 72.65*; H, 13.04*; N, 14.30; neut. equiv., 109.2, 116.6*.

Lukeš and Přeučil[10] report a dibromo hydrobromide melting at 191°. Careful bromination of the amine in chloroform gave a water-soluble solid, which after recrystallization from ethanol formed colorless needles, m. p. 193–194°.

The picrate melted at 110.9–111.8°. The compound shows dimorphism: when the sample melted on the block was touched with a spatula it solidified and remelted at 114–114.2°.

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 43.90; H, 4.91. Found: C, 43.98; H, 5.18.

The methiodide separated when a solution of the amine and methyl iodide in ether was allowed to stand. It crystallized from chloroform containing a little alcohol as long, hygroscopic needles, m. p. 240–241.3°.

Anal. Calcd. for $C_7H_{16}IN$: C, 34.87; H, 6.69. Found: C, 35.00; H, 6.98.

α,α-Diallylbenzylamine.—The general procedure of Henze, Allen and Leslie was followed. To an ether solution of 1.6 moles of allylmagnesium bromide was gradually added 77.8 g. (0.75 mole) of benzonitrile. The mixture was refluxed for several hours, during which time a green solid separated. After hydrolysis of the reaction mixture with iced ammonium chloride and extraction of the tarry product with dilute acid, there was isolated 15 g. of the crude unsaturated amine, b. p. 75–89° at 0.75–1.0 mm. This was redistilled; the fraction boiling at 87.5–90.0° (0.75 mm.) weighed 11 g., and had $n^{25}D$ 1.5310.

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.30; H, 9.52.

The picrate of α,α-diallylbenzylamine was prepared by the addition of ethereal picric acid (0.24 g.) to an ether solution of the amine (0.2 ml.). It formed fine yellow needles which melted at 126°, then resolidified and remelted at 133°. After recrystallization from chloroform–methanol it melted at 134.0–134.5°.

Anal. Calcd. for $C_{19}H_{20}N_4O_7$: C, 54.82; H, 4.81; N, 13.46. Found: C, 54.11, 54.15*; H, 5.04, 4.75*; N, 13.39*.

The benzenesulfonamide of α,α-diallylbenzylamine was prepared by warming equal quantities (*ca.* 0.2 g.) of the amine and benzenesulfonyl chloride with 2 ml. of 6 *N* sodium hydroxide on the steam-bath for ten minutes. The product separated as the reaction progressed and appeared to be alkali-insoluble. It was recrystallized from dilute alcohol, forming white needles, m. p. 151–152°.

Anal. Calcd. for $C_{16}H_{21}NO_2S$: C, 69.69; H, 6.47. Found: C, 69.50; H, 6.75.

The alkali-insolubility of the derivative recalls the alkali-insolubility of highly ortho-substituted phenols.

The thiourea derivative of α,α-diallylbenzylamine was prepared by warming equal amounts of the amine and phenyl isothiocyanate on the steam-cone for several minutes. The reaction mixture was dissolved in hot alcohol, from which colorless needles separated on cooling. The melting point of this product was 142–143°, but after recrystallization from dilute alcohol it had m. p. 132.5–133.5°. The melted (133°) sample was cooled and scratched, forming a solid which melted at 142°. Recrystallization from benzene–ligroin gave the low-melting form.

Anal. Calcd. for $C_{20}H_{22}N_2S$: C, 74.49; H, 6.88. Found: C, 74.66; H, 7.12.

The Reaction of α,α-Diallylbenzylamine with Formaldehyde.—A mixture of 3.0 g. (0.016 mole) of α,α-diallylbenzylamine, 10 ml. of 6 *N* sulfuric acid, 3 ml. of 36–38% formalin and 100 ml. of water was distilled until about 35 ml. of distillate had been collected. The two-phase distillate was extracted with ether, the ether solution dried over potassium carbonate and the solvent evaporated. The colorless liquid residue (1.3 g.) rapidly decolorized potassium permanganate solution and reacted with 2,4-dinitrophenylhydrazine (see below).

The acidic residue from the steam distillation was made alkaline and steam distilled into two fractions of about 3 ml. each. Both were two-phase mixtures and both had the intense odor characteristic of 3-butenylamine.

The picrate was prepared from the amine contained in

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[9] Ciamician and Magnaghi, *Ber.*, **18**, 2080 (1885), report the boiling point of this compound, which they called "dimethyl pyrrolidine," as 89–92°.

[10] Lukeš and Přeučil, *Coll. Czech. Chem. Comm.*, **10**, 384 (1938).

the first of these two fractions. It melted at 137.5–138° after recrystallization from chloroform–methanol. A mixed m. p. with the 3-butenylamine obtained from α-allylbenzylamine (m. p. 137.5–138°) was unchanged.

Allyl Phenyl Ketone 2,4-Dinitrophenylhydrazone.—The neutral material obtained by steam distillation of the acidic solution described in the preceding section reacted with 2,4-dinitrophenylhydrazine to give what appeared to be a mixture. From 0.4 g. of the ketone and 0.54 g. of 2,4-dinitrophenylhydrazine was obtained 0.8 g. of orange-red plates melting at about 170°. Repeated recrystallization of this material from alcohol–acetic acid, glacial acetic acid and finally dilute acetic acid yielded large, shining orange-red leaflets, m. p. 201–203°.

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32. Found: C, 59.06; H, 4.32.

There was also obtained a small amount of deep red material, m. p. 190–195°. This was evidently still impure and was obtained in too small an amount to permit of further purification and analysis.

Reduction of Allyl Phenyl Ketone.—A mixture containing 0.41 g. of allyl phenyl ketone and 25 mg. of platinum oxide in 15 ml. of absolute ethanol was shaken with hydrogen at about 2 atmospheres pressure. The reduction was stopped when one mole of hydrogen had been absorbed.

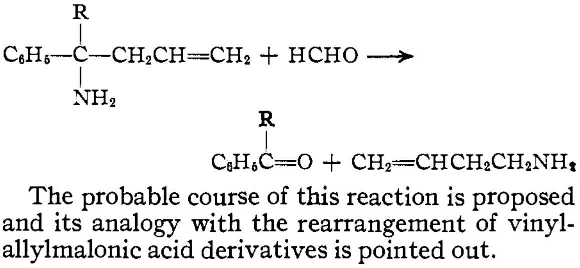
The filtered solution was divided into two equal portions. One of these was treated with 0.25 g. of 2,4-dinitrophenylhydrazine in alcohol containing a trace of hydrochloric acid. The derivative formed orange-red platelets, m. p. 189–190°. An authentic sample of *n*-butyrophenone was treated in the same way to yield a product melting at 190–191°. The mixed melting point was 189.5–190°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.52; H, 4.91. Found: C, 58.41; H, 5.01.

The second portion of the solution from the hydrogenation was used to prepare the semicarbazone. This melted at 180–181°, and a mixed melting point with an authentic sample (m. p. 180–181°) melted at 180–181°. Huntress and Mulliken[11] give m. p. 187–188° and 191.5°; McElvain[12] gives m. p. 184° for this derivative.

Summary

α-Allylbenzylamine and α,α-diallylbenzylamine react with formaldehyde with rearrangement and cleavage according to the general reaction



$$C_6H_5-\overset{R}{\underset{NH_2}{C}}-CH_2CH=CH_2 + HCHO \longrightarrow C_6H_5\overset{R}{C}=O + CH_2=CHCH_2CH_2NH_2$$

The probable course of this reaction is proposed and its analogy with the rearrangement of vinylallylmalonic acid derivatives is pointed out.

(11) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

(12) McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 20, 1949

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

3-Phenylindones. I. The Synthesis of 6-Chloro-3-(*p*-chlorophenyl)-1-indenone and Some Related Compounds[1]

BY JAMES F. FEEMAN[2,3] AND E. D. AMSTUTZ

Although it is extremely difficult if not impossible, on the basis of present knowledge, to predict the insecticidal properties of a given compound, it has been noted[4] that certain structural groups appear in many of the most potent and useful insecticides. Thus, we concluded that substitution of the conjugated system –C=C–C=O for the trichloroethane grouping in the DDT molecule, either as a fused ring system, or in the form of a substituted acrylic ester, might be expected to produce compounds of value as selective insecticides. The investigations described here were concerned with the synthesis of the 3-phenylindone structurally related to DDT, and of several related reduction and halogenation products. Several of the intermediate di-(*p*-chlorophenyl)-acrylic, hydracrylic and propionic acids and esters are also of interest, both as possible insecticidal agents and as phytotoxic materials.

The sequence of reactions employed in the synthesis of this series of compounds has been outlined in the formula diagram. With 4,4′-dichlorobenzophenone as the starting compound, a Reformatsky reaction with either methyl or ethyl bromoacetate, employing the modification of Fieser and Johnson[5] for the preparation of active zinc, and following the suggestion of Hussey and Newman[6] for the improvement of yields by use of excess zinc and bromoester, yielded the corresponding hydracrylic esters (II, III) in over 90% yield. Difficulties encountered in separation of the unreacted dichlorobenzophenone from the esters, by means of fractional crystallization, led to direct saponification of the crude reaction product. This allowed ready separation of the β,β-bis-(*p*-chlorophenyl)-hydracrylic acid (IV). The ethyl ester has been prepared previously by means of a similar reaction.[7]

(1) Abstracted from the dissertation of James F. Feeman, presented to the faculty of the Graduate School of Lehigh University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1949.

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(4) Frear, "A Catalogue of Insecticides and Fungicides, Vol. I. Chemical Insecticides," Chronica Botanica Company, Waltham, Mass., 1947.

(5) Fieser and Johnson, THIS JOURNAL, **62**, 575 (1940).

(6) Hussey and Newman, *ibid.*, **70**, 3024 (1948).

(7) Bergmann, Hoffmann and Meyer, *J. prakt. Chem.*, **135**, 245 (1932).