anhydrous hydrogen chloride to the ether solution gave 1-(*p*-methoxyphenyl)-2-methyl-2-propylamine hydrochloride.

1-(2′-Nitro-4′-hydroxyphenyl)-2-methyl-2-nitropropane.—1-(2′-Nitro-4′-aminophenyl)-2-methyl-2-nitropropane (6.0 g., 0.025 mole) was added to a boiling solution of 12 ml. of 37% hydrochloric acid (0.145 mole) and 38 ml. of water. When complete dissolution was accomplished, the solution was cooled to 5°. Sodium nitrite (2.0 g., 0.030 mole) dissolved in 10 ml. of water was added dropwise with stirring. The cold diazonium solution was added slowly to the bottom of a solution of 3 ml. of 96% sulfuric acid in 200 ml. of water covered with a layer of xylene. The solution was stirred intermittently, the temperature being maintained at 95°. The xylene layer was separated and extracted with 5% sodium hydroxide. The alkaline solution was acidified and extracted with ether. The ether extract was treated with Norit, dried and evaporated under reduced pressure. The residue was recrystallized from benzene–petroleum ether (60–70°) giving 1-(2′-nitro-4′-hydroxyphenyl)-2-methyl-2-nitropropane; yield 2.0 g. (33%), m.p. 75–76°.

Anal. Calcd. for $C_{10}H_{12}N_2O_5$: N, 11.62. Found: N, 11.68.

1-(2′-Amino-4′-hydroxyphenyl)-2-methyl-2-propylamine Dihydrochloride.—1-(2′-Nitro-4′-hydroxyphenyl)-2-methyl-2-nitropropane (2.0 g., 0.008 mole) was reduced with Raney nickel and hydrogen. The diamine was converted to its hydrochloride salt. This salt is extremely hygroscopic and was dried at 80° under vacuum; heating to higher temperatures caused decomposition of the material. Two molecules of water of crystallization were retained.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

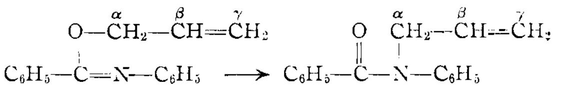
The Rearrangement of N-Phenylbenzimidoyl γ,γ-Dimethylallyl Ether

BY W. M. LAUER AND ROBERT G. LOCKWOOD[1]

RECEIVED MARCH 20, 1954

The N-phenylbenzimidoyl allyl ethers, which have been studied previously, undergo rearrangement to form N-allylbenzanilides. Migration of the allyl group from the oxygen to nitrogen occurs with inversion. The present study describes the rearrangement of N-phenylbenzimidoyl γ,γ-dimethylallyl ether; in this case migration of the γ,γ-dimethylallyl group takes place without inversion and instead of becoming attached to the nitrogen, the group enters an *ortho* position of the aromatic nucleus.

The transformation of N-phenylbenzimidoyl allyl ether (I) to N-allylbenzanilide (II), described in 1937 by Mumm and Möller[2] bears considerable resemblance to the phenyl allyl ether rearrangement.

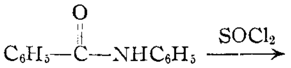


$$\underset{\text{I}}{C_6H_5-\overset{\displaystyle O-\overset{\alpha}{C}H_2-\overset{\beta}{C}H=\overset{\gamma}{C}H_2}{\overset{|}{C}}=N-C_6H_5} \longrightarrow \underset{\text{II}}{C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle \overset{\alpha}{C}H_2-\overset{\beta}{C}H=\overset{\gamma}{C}H_2}{\overset{|}{N}}-C_6H_5}$$

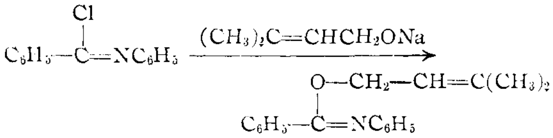
For example, these investigators were able to demonstrate that inversion of the α- and the γ-methylallyl group occurs in this transformation. Thus, N-phenylbenzimidoyl *α-methyl*allyl ether on heating yielded N-*γ-methyl*allylbenzanilide and N-phenylbenzimidoyl *γ-methyl*allyl ether gave N-*α-methyl*-allylbenzanilide.

In order to obtain further information concerning the similarity of this transformation and the phenylallyl ether rearrangement it was of interest to learn whether some of the abnormal phenyl allyl ether rearrangements, previously described,[3] are duplicated in the case of the N-phenylbenzimidoyl allyl ethers. N-Phenylbenzimidoyl γ,γ-dimethylallyl ether was chosen for this study since no normal rearrangement product was obtained in the case of the γ,γ-dimethylallyl ether of ethyl *p*-hydroxybenzoate.

N-Phenylbenzimidoyl γ,γ-dimethylallyl ether (III) was obtained as a result of the following series of reactions



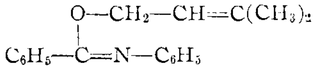
$$C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-NHC_6H_5 \xrightarrow{SOCl_2}$$



$$C_6H_5-\overset{\displaystyle Cl}{\overset{|}{C}}=NC_6H_5 \xrightarrow{(CH_3)_2C=CHCH_2ONa} \underset{\text{III}}{C_6H_5-\overset{\displaystyle O-CH_2-CH=C(CH_3)_2}{\overset{|}{C}}=NC_6H_5}$$

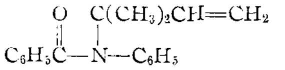
γ,γ-Dimethylallyl bromide, prepared by the addition of hydrogen bromide to isoprene, was converted to the corresponding acetate. Hydrolysis of the acetate yielded γ,γ-dimethylallyl alcohol. N-Phenylbenzimidoyl chloride in benzene solution, treated with sodium γ,γ-dimethylallyl oxide gave the desired ether, N-phenylbenzimidoyl γ,γ-dimethylallyl ether (III). This ether on hydrolysis gave the expected products, benzoic acid, aniline and γ,γ-dimethylallyl alcohol.

Pyrolysis of the liquid ether led to the formation of a solid rearrangement product in excellent yield. At the outset three structures (IV, V and VI) were considered as likely possibilities for the product of rearrangement. They were the following substituted N-allylbenzanilides.



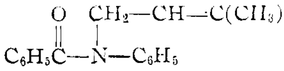
$$C_6H_5-\overset{\displaystyle O-CH_2-CH=C(CH_3)_2}{\overset{|}{C}}=N-C_6H_5$$

III



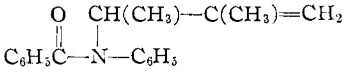
$$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle C(CH_3)_2CH=CH_2}{\overset{|}{N}}-C_6H_5$$

IV



$$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CH_2-CH=C(CH_3)_2}{\overset{|}{N}}-C_6H_5$$

V



$$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CH(CH_3)-C(CH_3)=CH_2}{\overset{|}{N}}-C_6H_5$$

VI

However, as the study progressed it became evident that none of these structures was the correct one and that instead of oxygen to nitrogen migration of the substituted allyl group, this group be-

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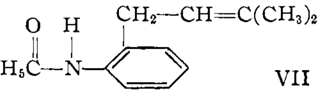
[1] From the Ph.D. Thesis of R. G. Lockwood submitted in June, 1953.

[2] O. Mumm and F. Möller, *Ber.*, **70**, 2214 (1937).

[3] *Inter alia* (a) W. M. Lauer and W. Filbert, THIS JOURNAL, **58**, 1388 (1936); (b) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939); (c) W. M. Lauer and O. Moe, THIS JOURNAL, **65**, 289 (1943).

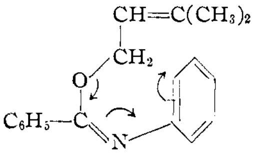
came attached to the *ortho* position of the aromatic nucleus. Infrared absorption data[4] were shown to be inconsistent with N-allylic benzanilide structures (IV, V and VI) by comparison of the infrared absorption curves of the rearrangement products, N-allylbenzanilide and N-(γ,γ-dimethylallyl)-benzanilide (V). The latter two compounds exhibited strong absorption at 1650–1660 cm.$^{-1}$, which is characteristic of disubstituted amides, but this band did not appear in the case of the rearrangement product. Instead, it showed moderate absorption at 3400 cm.$^{-1}$, which is the stretching frequency of either an –OH or >NH bond; this band was missing in the case of the disubstituted amides. Because of the presence of bands at 1590 and 1695 cm.$^{-1}$, as well as the >NH stretching band at 3400 cm.$^{-1}$, the rearrangement product was regarded as a monosubstituted amide. Ozonolysis of the rearrangement product yielded acetone and oxidation with potassium permanganate of the non-volatile component of the ozonization product produced N-benzoylanthranilic acid.

Hydrolysis of the rearrangement product using an ethylene glycol solution of potassium hydroxide yielded a substituted aniline. That there was no shift of the double bond during hydrolysis was established by treatment with benzoyl chloride to give the original substituted benzanilide. Catalytic hydrogenation proceeded with the uptake of two hydrogen atoms. Hydrolysis of this hydrogenated product likewise yielded a substituted aniline, which on the basis of a Hinsberg test and coupling studies was shown to be primary. On the basis of these findings the rearrangement product was assigned the structure

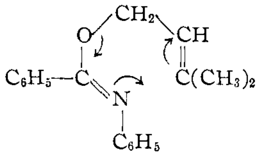


VII

The formation of *o*-benzamido-γ,γ-dimethylallylbenzene (VII) by the rearrangement of N-phenylbenzimidoyl γ,γ-dimethylallyl ether (III) resembles the *para* rearrangement of phenyl allyl ethers, since non-inversion of the allyl group characterizes each of these processes.[5] The mechanism of the rearrangement of N-phenylbenzimidoyl γ,γ-dimethylallyl ether (III) could follow the course postulated for the *p*-Claisen rearrangement[6] involving two cyclic (6-ring) transition states of which B is the first; hence a double inversion occurs. In the case under study a single six-membered cyclic transition state of type A, which also would lead to non-inversion, appears more likely.



A



B

A cyclic transition state of type B is apparently involved in the previously described cases in which the allylic group migrates with inversion to the nitrogen. In the present case steric factors appear to play a determining role, directing the migrating allylic group to the *ortho* position without inversion.

Experimental

N-Phenylbenzimidoyl chloride was prepared according to the method of von Braun and Pinkernelle.[7]

The product, on exposure to the atmosphere, slowly deposited benzanilide. It was conveniently stored in dry benzene.

γ,γ-Dimethylallyl bromide was prepared by the addition of hydrogen bromide in glacial acetic acid to isoprene according to the method of Staudinger, Kreis and Schilt.[8]

γ,γ-Dimethylallyl acetate was obtained by utilizing the procedures of Meisenheimer and Link,[9] and Meisenheimer and Beutter.[10] Treatment of the acetate (173 g., 1.33 moles) with a solution of sodium hydroxide (108 g.) in water (432 ml.), gave the **γ,γ-dimethylallyl alcohol** (99 g., b.p. 139–141.5°, n^{20}_{D} 1.4442). The phenylurethan, after one crystallization from petroleum ether, melted at 63–63.5° in agreement with recorded values.[11]

N-Phenylbenzimidoyl γ,γ-Dimethylallyl Ether (III).—Sodium γ,γ-dimethylallyl oxide was prepared by the reaction of sodium (9.9 g.) in dry thiophene-free benzene (150 ml.) with a solution of γ,γ-dimethylallyl alcohol (37.5 g.) in benzene (50 ml.). The allyl oxide suspension was cooled slightly, and a solution of N-phenylbenzimidoyl chloride (92.2 g.) in benzene (150 ml.) was added, with stirring, at such a rate that the benzene refluxed gently. Stirring and heating under reflux on the steam-bath were continued for two hours. The mixture was cooled to room temperature and filtered. The filtrate was distilled on the steam-bath to remove the benzene. The dark, viscous residue was then distilled *in vacuo;* the imido ether (43 g.) was collected at 131–135° (0.15 mm.) with a maximum temperature of the heating bath at 195°. A sample of the ether (n^{25}_{D} 1.5738) was analyzed.

Anal. Calcd. for $C_{18}H_{19}ON$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.57; H, 7.06; N, 5.52.

Hydrolysis of N-Phenylbenzimidoyl γ,γ-Dimethylallyl Ether (III).—The ether (13.3 g., 0.05 mole) was heated under reflux for 11 hours with a solution of potassium hydroxide (5.6 g., 0.1 mole) in ethanol (60 ml.). The ethanol was then removed by distillation and replaced by an equal volume of ether. The ether solution was extracted three times with 30-ml. portions of water. The combined aqueous extracts after acidification with dilute hydrochloric acid yielded a small amount (0.2 g.) of benzoic acid. Since only a small amount of benzoic acid was obtained, the hydrolysis was continued. The combined ether solutions were evaporated to an orange oil, which was then heated under reflux as before with potassium hydroxide (11.2 g.) in ethanol (70 ml.). The mixture was worked up in the previously described manner and an additional amount (0.5 g.) of benzoic acid was obtained.

Evaporation of the ether solution again produced an orange oil. Distillation of this oil gave colorless γ,γ-dimethylallyl alcohol (0.8 g., 19%, collected at 135–145°, n^{20}_{D} 1.4503) and aniline (1.0 g., b.p. 184–195°, n^{20}_{D} 1.5705). The residue (7.5 g.) consisted of rearranged imido ether, which solidified on cooling.

The γ,γ-dimethylallyl alcohol was identified as the phenylurethan and the aniline was identified by its conversion to benzanilide.

Rearrangement of N-Phenylbenzimidoyl γ,γ-Dimethylallyl Ether.—The pure imido ether (29.6 g.) was placed in

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[4] We are indebted to Dr. Stuart W. Fenton and Dr. Bryce Crawford, Jr., for these spectra and their interpretation.

[5] (a) O. Mumm and F. Möller, ref. 2; (b) O. Mumm, H. Hornhardt and J. Diederichsen, *Ber.*, **72**, 100 (1939); (c) O. Mumm and J. Diederichsen, *ibid.*, **72**, 1523 (1939); (d) J. P. Ryan and P. R. O'Connor, THIS JOURNAL, **74**, 5866 (1952); (e) S. J. Rhoads, R. Raulins and R. D. Reynolds, THIS JOURNAL, **75**, 2531 (1953); (f) E. N. Marvell and R. W. Ledeen, Abs. of Chicago meeting of the A.C.S. 1953, p. 84.

[6] (a) See especially C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939); (b) H. Conroy and R. A. Firestone, THIS JOURNAL, **75**, 2530 (1953).

[7] J. v. Braun and W. Pinkernelle, *Ber.*, **67**, 1218 (1934).

[8] H. Staudinger, W. Kreis and W. Schilt, *Helv. Chim. Acta*, **5**, 743 (1922).

[9] J. Meisenheimer and J. Link, *Ann.*, **479**, 211 (1930).

[10] J. Meisenheimer and G. Beutter, *ibid.*, **508**, 58 (1934).

[11] W. G. Young and I. D. Webb, THIS JOURNAL, **73**, 780 (1951).

an erlenmeyer flask fitted with an 8 mm. air condenser approximately 20 cm. in length. The contents of the flask were brought to a temperature of 255–260° (Wood's metal-bath). The imido ether suddenly boiled; the flask was removed from the bath and ebullition continued for a short time. For the remainder of the heating period (2 hr. total), the bath was held at 220–225°.

The dark amber liquid solidified readily when allowed to cool. After a single crystallization (Norite) from aqueous ethanol the rearrangement product was obtained as small colorless needles, m.p. 118–119° in 75% yield. Recrystallization from ethanol gave a pure sample, m.p. 120–121°. Evaporation of the mother liquors yielded additional product.

Anal. Calcd. for $C_{18}H_{19}ON$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.63; H, 7.30; N, 5.47.

Hydrogenation of Rearrangement Product.—The rearrangement product (4.9 g.) was hydrogenated (50 p.s.i.) in alcohol (100 ml.) using platinum oxide catalyst. Colorless needles (4.3 g., 87%, m.p. 154–154.5°) were obtained.

Anal. Calcd. for $C_{18}H_{21}ON$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.60; H, 7.73; N, 5.45.

Hydrolysis of *o*-Benzamidoisoamylbenzene.—The amide (18.0 g.) was added to a hot solution of potassium hydroxide (10.0 g.) in ethylene glycol (50 ml.) and the yellow mixture was heated under reflux for three hours. Crystals (potassium benzoate) of a water-soluble salt deposited on cooling. After the addition of water (100 ml.), the two-phase mixture was extracted with ether and the combined ether extracts were dried over magnesium sulfate. Distillation yielded the colorless amine (9.8 g., 89%, b.p. 128–131° at 15 mm.). A middle fraction ($n^{25}D$ 1.5310) was analyzed.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.66; H, 10.33; N, 8.75.

This substituted aniline was shown to be primary by the Hinsberg test with benzenesulfonyl chloride and by the formation of a dye when the diazotized aniline was coupled with phenol or β-naphthol. The substituted aniline was readily benzoylated to give *o*-benzamidoisoamyl benzene (m.p. 153–154.5°; mixed m.p. with material before hydrolysis was unchanged).

Hydrolysis of *o*-Benzamido-γ,γ-dimethylallylbenzene.—The rearrangement product (18.0 g.) was hydrolyzed under the same conditions used for the hydrolysis of *o*-benzamidoisoamylbenzene. The colorless amine (9.2 g., 84%) was collected at 137–138° (16 mm.) and a middle fraction ($n^{25}D$ 1.5550) was analyzed.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69 Found: C, 81.88; H, 9.21; N, 8.75.

The double bond did not shift into conjugation with the aromatic nucleus during alkaline hydrolysis, since benzoylation of the amine gave the starting material (m.p. 120–121° after one crystallization from aqueous ethanol; mixed m.p. with rearrangement product 119–120°).

The amine, *o*-(γ,γ-dimethylallyl)-aniline, was converted through the diazonium salt to the corresponding bromo compound, which was in turn oxidized with potassium permanganate to *o*-bromobenzoic acid, m.p. and mixed m.p. 148°. These results were regarded as inconclusive on account of the low yields.

Ozonolysis of *o*-Benzamido-γ,γ-dimethylallylbenzene.—The rearrangement product (2.0 g.) in ethyl acetate (60 ml.) was ozonized at the temperature of an ice-bath. After saturation with ozone, the ethyl acetate solution was transferred to a dropping funnel and the major portion of the ethyl acetate was removed under reduced pressure at room temperature. The yellow residue (5–7 ml.) was added dropwise to a refluxing mixture of water (50 ml.), acetic acid (1 ml.) and zinc dust (1.5 g.). As the ozonide decomposed, an oily residue was formed and the volatile components were distilled directly into freshly prepared 2,4-dinitrophenylhydrazine reagent (prepared from 1.5 g. of the solid reagent, 2 ml. of concd. sulfuric acid, 3 ml. of water and 15 ml. of ethanol). Yellow-orange needles (0.65 g., 36%) of acetone 2,4-dinitrophenylhydrazone (m.p. 124–124.5°) were formed. One recrystallization from aqueous ethanol gave a product, m.p. and mixed m.p. 126–127°.

The viscous, non-volatile residue from the decomposition of the ozonide was extracted with ether and the ether extract was concentrated on the steam-bath. The residue was then heated under reflux with potassium permanganate (2.5 g. in 48 ml. water). The permanganate solution was added portionwise over a period of one-half hour until the color ceased to fade. The mixture was then cooled, acidified with sulfuric acid (20%) and treated with sodium bisulfite. Light-tan needles (m.p. 170–183°, 298 mg., 48%) were obtained. Crystallization from benzene yielded N-benzoylanthranilic acid, m.p. and mixed m.p. 180–181.5°.

N-(γ,γ-Dimethylallyl)-aniline.—A mechanically stirred, warm solution of formanilide (18.1 g., m.p. 47–49°), γ,γ-dimethylallyl bromide (22.4 g.) and ethanol (40 ml.) was treated with a solution of potassium hydroxide (8.7 g.) in ethanol (70 ml.). The mixture was stirred and heated under reflux on the steam-bath for one hr., after which it was cooled and the salt collected on a filter. The filtrate was concentrated to a volume of 25 ml. and hydrolyzed with ethanolic potassium hydroxide. Ether extraction followed by distillation gave aniline (8.0 g.) and N-(γ,γ-dimethylallyl)-aniline (2.0 g., b.p. 132–138° at 13 mm., $n^{25}D$ 1.5518).

The *p*-toluenesulfonamide (m.p. 81–81.5°) was prepared.

Anal. Calcd. for $C_{18}H_{21}O_2NS$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.61; H, 6.79; N, 4.50.

N-(γ,γ-Dimethylallyl)-benzanilide (m.p. 83–83.5°) was obtained by the usual benzoylation procedure.

Anal. Calcd. for $C_{18}H_{19}ON$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.46; H, 7.34; N, 5.28.

Claisen[12] reported 80–81° for the melting point of this compound.

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[12] L. Claisen, *J. prakt. Chem.*, **105**, 65 (1922).