EXPERIMENTAL

Compounds investigated. Most of the hydroxamic acids used in this study were prepared by procedures already described in the literature.[5]

N-Methyl benzohydroxamic acid and its *p*-methoxy derivatives were prepared by the reaction of benzoyl and anisoyl chloride, respectively, with *N*-methylhydroxylamine. *N*-Methylbenzohydroxamic acid was a colorless liquid which boiled at 103–105° at 0.6 mm.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.5; H, 5.95; N, 9.3. Found: C, 63.1; H, 6.1; N, 9.7.

p-Methoxy-*N*-methylbenzohydroxamic acid melted at 108°.

Anal. Calcd. for $C_9H_{11}NO_3$: C, 59.7; H, 6.1. Found: C, 60.2; H, 6.2.

trans-Crotonohydroxamic acid was synthesized from crotyl chloride and hydroxylamine and melted at 116°.

Anal. Calcd. for $C_4H_7NO_2$: C, 47.5; H, 6.9. Found: C, 47.4; H, 6.9.

Spectra. The ultraviolet absorption spectra were determined by means of a Beckman Quartz DU Photoelectric spectrophotometer or a Cary Spectrophotometer. Solutions of the hydroxamic acids (*ca.* 5.8 × 10^{-5} molar) were made up in 0.1*N* hydrochloric acid and 0.005*N* sodium hydroxide except as noted in Tables I and II. To minimize decomposition of the hydroxamic acids, the solution was made alkaline just prior to use.

Acknowledgment. The author wishes to express gratitude to Mr. Omer O. Owens for preparing some of the compounds used in this investigation. The author also wishes to thank the Analytical Research Branch of these Laboratories for the use of their Cary recording spectrophotometer.

ARMY CHEMICAL CENTER, MD.

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(5) Benzohydroxamic acid—W. B. Renfrew and C. R. Hauser, *J. Am. Chem. Soc.*, **59**, 2312 (1957); *p*-substituted benzohydroxamic acids—B. E. Hackley, Jr., R. E. Plapinger, M. Stolberg, and T. Wagner-Jauregg, *J. Am. Chem. Soc.*, **77**, 3651 (1955); ethylsynbenzhydroximic acid—E. Eiseler, *Ann.*, **175**, 328 (1875) and O. Gurke, *Ann.*, **205**, 285 (1905); sorbohydroxamic acid—G. M. Steinberg and J. Bolger, *J. Org. Chem.*, **21**, 660 (1956); and *O*-methylbenzohydroxamic acid—W. Lossen, *Ann.*, **281**, 186 (1894).

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

Rearrangement of *N*-Phenylbenzimidoyl γ-Ethylallyl Ether

W. M. LAUER AND C. S. BENTON[1]

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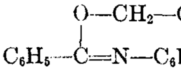
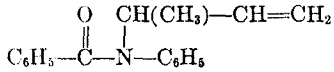
Thermal rearrangement of *N*-phenylbenzimidoyl γ-ethylallyl ether leads to the formation of *N*-ethylvinylcarbinyl benzanilide. Thus, migration of the γ-ethylallyl group from the oxygen to nitrogen occurs with inversion. At somewhat higher temperatures this initial pyrolysis product rearranges to *o*-benzamido-γ-ethylallylbenzene. This nitrogen to carbon migration also proceeds with inversion.

Relatively few *N*-phenylbenzimidoyl allyl ethers have been rearranged. Mumm and Möller[2] demonstrated that *N*-phenylbenzimidoyl γ-methylallyl ether (I) rearranges with inversion to produce *N*-α-methylallyl benzanilide (II). In order to obtain further information concerning the similarity of this transformation and the Claisen rearrangement, Lauer and Lockwood[3] studied the pyrolysis of *N*-phenylbenzimidoyl γ,γ-dimethylallyl ether, III. No normal rearrangement product had been obtained in the case of the γ,γ-dimethylallyl ether of ethyl *p*-hydroxybenzoate[4] and likewise, no shift of the γ,γ-dimethylallyl group from oxygen to nitrogen occurred in the case of *N*-phenylbenzimidoyl γ,γ-dimethylallyl ether. Instead, the migrating γ,γ-dimethylallyl group became attached to the aromatic nucleus without inversion, and the structural change was represented as follows:



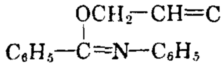
$C_6H_5-\overset{O-CH_2-CH=CHCH_3}{\overset{|}{C}}=N-C_6H_5$

I



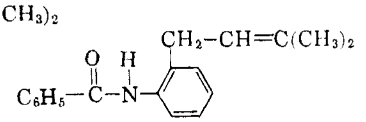
$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{CH(CH_3)-CH=CH_2}{\overset{|}{N}}-C_6H_5$

II



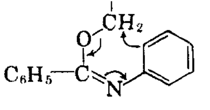
$C_6H_5-\overset{OCH_2-CH=C(CH_3)_2}{\overset{|}{C}}=N-C_6H_5$

III



IV

This process can be viewed as a double inversion; the first step involving migration from oxygen to nitrogen and the second from nitrogen to carbon. A first step of this kind might be expected to be hindered by steric factors. No normal migration of the γ,γ-dimethylallyl group with inversion occurs in the Claisen rearrangement and therefore by analogy such a step might be considered to be unlikely. A single six-membered cyclic transition state of type A, which would not require oxygen to nitrogen migration with inversion, can be postulated.



A

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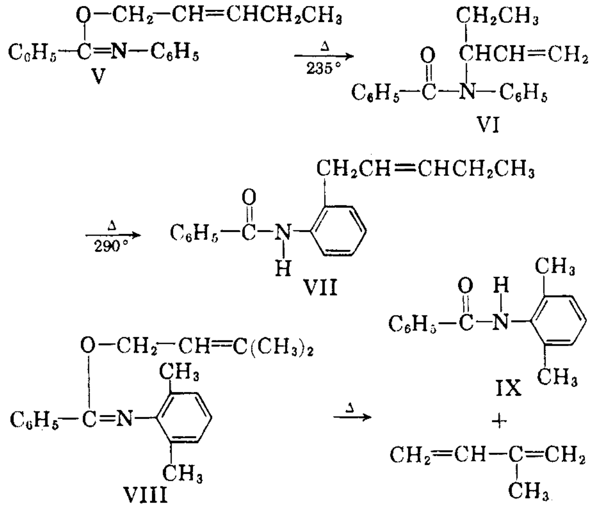
(1) From the Ph.D. Thesis of C. S. Benton submitted in August 1957.

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

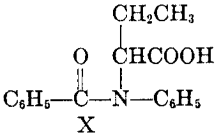
(3) W. M. Lauer and R. G. Lockwood, *J. Am. Chem. Soc.*, **76**, 3974 (1954).

(4) W. M. Lauer and O. Moe, *J. Am. Chem. Soc.*, **65**, 289 (1943).

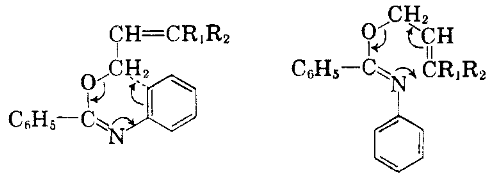
In the present study two N-phenylbenzimidoyl substituted allyl ethers were pyrolyzed. One, N-phenylbenzimidoyl γ - ethylallyl ether (V), in which oxygen to nitrogen migration is more probable than in III and N-2,6-dimethylphenylbenzimidoyl γ,γ-dimethylallyl ether (VIII), in which migration into the aromatic nucleus is hindered and in which, perhaps, oxygen to nitrogen migration may occur. The results of this study can be described by means of the following equations.



N-ethylvinylcarbinylbenzanilide (VI) was degraded to N-phenyl-N-benzoyl-α-aminobutyric acid (X), which was synthesized starting with ethyl α-bromo-n-butyrate. o-Benzamido-γ-ethylallylbenzene (VII) was degraded to N-benzoyl anthranilic acid and propionaldehyde, which was identified as its 2,4-dinitrophenylhydrazone. Benz-2,6-dimethylanilide (IX) was identified by means of its melting point and infrared spectrum. The above equations represent the main products which are produced on pyrolysis. Certainly, in the case of N-phenylbenzimidoyl γ-ethylallyl ether (V), oxygen to nitrogen migration with inversion, followed by a second migration from nitrogen to the aromatic nucleus with inversion can occur. However, the cases of N-2,6-dimethylphenylbenzimidoyl γ,γ-dimethylallyl ether (VIII) and N-phenylbenzimidoyl $\gamma\gamma$-dimethylallyl ether do show that there is little or no tendency for the γ,γ-dimethylallyl group to undergo oxygen to nitrogen migration. Apparently, migration of this group with normal inversion is beset with difficulty—a feature also manifested in the Claisen rearrangement. Therefore the following facts emerge. (a) N-Phenylbenzimidoyl γ-methylallyl ether (I) and the next higher homolog, N-phenylbenzimidoyl γ-ethylallyl ether (V), undergo oxygen to nitrogen migration with inversion of the γ-substituted allyl group. (b) There is no indication of a comparable oxygen to nitrogen migration in the case of N-phenylbenzimidoyl $\gamma\gamma$-dimethylallyl ether III, but instead oxygen to carbon migration occurs. (c) The product of oxygen to nitrogen migration (VI) in the case of the ether V is capable of undergoing nitrogen to carbon migration (with inversion). These findings become understandable if it is assumed that the two transition states A and B are in competition, and if assignment of determinative power is made to the steric effect of the γ-substituents, R_1 and R_2, in the allyl group.



X



A B

In the limiting sense, it can be argued that, where the intermediate resulting from transition state B cannot be isolated, its rate of decomposition must be as fast as its rate of formation, so that there is no necessity for postulating its existence at all. Thus, in the case in which $R_1 = R_2 = CH_3$, there appears to be no present justification for postulating a double migration with inversion at each step.

EXPERIMENTAL

N-Phenylbenzimidoyl γ-ethylallyl ether (V). Ethylvinyl carbinol (b.p. 110–113° at 735 mm.; n_D^{20} 1.4233) was obtained by the action of ethylmagnesium bromide on freshly distilled acrolein. The carbinol was next transformed to *γ-ethylallyl chloride* (b.p. 103–110°; n_D^{20} 1.4372) by means of thionyl chloride. The chloride was then added slowly to glacial acetic acid containing fused potassium acetate and heated under reflux for 4 hr. After the reaction mixture was poured into ice water, extraction with ether yielded *γ-ethylallyl acetate* (b.p. 142–152°). Saponification of this ester (10% aq. NaOH and ethanol) gave *γ-ethylallyl alcohol* (b.p. 138–139°; n_D^{20} 1.4347). *N-Phenylbenzimidoyl chloride* was obtained by heating benzanilide and thionyl chloride under reflux with stirring for 4 hr. The greenish reaction mixture was then distilled (b.p. 190–210° at 15–20 mm.). The clear yellow chloride (m.p. 39–39.5°) solidified on cooling and was obtained in 95% yield.

N-Phenylbenzimidoyl γ-ethylallyl ether (V) was prepared by the action of sodium γ-ethylallyloxide on N-phenylbenzimidoyl chloride. The γ-ethylallyl alcohol was treated in benzene solution with sodium sand in an atmosphere of purified nitrogen. After the disappearance (*ca.* 10 hr.) of the metallic sodium, an equimolar amount of N-phenylbenzimidoyl chloride was added to the benzene solution. Stirring and heating in an atmosphere of nitrogen was continued for several hours and the reaction mixture was then allowed to stand. The benzene was removed by distillation and the material remaining was subjected to distillation under diminished pressure using a motor-driven pump. A small amount of γ-ethylallyl alcohol (b.p. 135° at 740 mm.; n_D^{20} 1.4358) was isolated from the forerun. Likewise, a small amount of benzanilide separated from the main fraction. It was removed by filtration and the yellow imido ether was redistilled (b.p. 150–155° at 0.005–0.01 mm.).

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.5; H, 7.22; N, 5.28. Found: C, 81.7; H, 7.25; N, 5.27.

Hydrolysis using methanolic potassium hydroxide gave benzoic acid, aniline and γ-ethylallyl alcohol (identified by means of b.p. and infrared spectrum).

The rearrangement of N-phenylbenzimidoyl γ-ethylallyl ether (V). Preliminary studies were conducted at 250° (7 hr.). The pyrolysis products were dissolved in benzene and then chromatographed on alumina. The two main products were (a) a compound (58% yield) with an infrared spectrum similar to that of *N*-allyl benzanilide which was shown to be *N*-ethylvinylcarbinyl benzanilide and (b) a compound (*ca.* 20%) with an infrared spectrum similar to that of *o*-benzamido-γ,γ-dimethylallylbenzene, which had been prepared earlier by Lauer and Lockwood. This second pyrolysis product was shown to be *o*-benzamido-γ-ethylallylbenzene. Subsequent studies showed that rearrangement at 235° yielded *N*-ethylvinylcarbinyl benzanilide which rearranged at 290° to give *o*-benzamido-γ-ethylallylbenzene (m.p. 110–110.5° Fisher-Johns melting block).

At 235°. The ether (V) was heated for 7 hr. under nitrogen in a tube immersed in a boiling diethylene glycol bath. The contents of the tube were then fractionally distilled. A sample of the middle fraction (120–125° at 0.03–0.05 mm.) was analyzed.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.5; H, 7.22. Found: C, 81.5, 81.5; H, 7.39, 7.20.

A sample of this rearrangement product, dissolved in ethyl acetate was subjected to ozonolysis at 0°. Hydrogen peroxide (200 ml. 3%) containing sodium hydroxide was then added and the resulting mixture was stirred. The aqueous layer was neutralized (Congo Red) with concd. hydrochloric and extracted with ether. The ether solution (positive peroxide test) was then extracted several times with aqueous sodium hydroxide (5%). Acidification followed by extraction with benzene, drying ($MgSO_4$), evaporation to a small volume and the addition of petroleum ether (b.p. 30–60°) produced crystalline degradation product. After several recrystallizations from benzene and petroleum ether the colorless product (m.p. 129–131° Fisher-Johns melting block) was analyzed.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C, 72.1; H, 6.05; N, 4.94. Found: C, 72.2, 72.4; H, 6.22, 6.22; N, 5.18, 5.19. Neutralization equivalent 281.

This degradation product, *N*-phenyl-*N*-benzoyl-α-aminobutyric acid was synthesized by treatment of ethyl α-bromobutyrate with aniline, condensing the resulting anilino compound with benzoyl chloride and saponifying the ester. The melting point (129–131° Fisher-Johns melting block) of the synthetic material was not changed by mixing with the degradation product. A comparison of the infrared spectra of the two samples showed no significant differences.

At 290°. Either the unrearranged ether (V), or the product of rearrangement at 235° (VI) when heated at 290° for 3 hr. in an atmosphere of nitrogen produced a solid. Purification by passage through a column of activated alumina, followed by elution with benzene containing a small amount of ethanol and by recrystallizing several times gave a product (m.p. 110–110.5°) which was analyzed.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.5; H, 7.22. Found: C, 81.4; H, 7.35.

Ozonolysis of this rearrangement product was carried out in ethyl acetate. After removal of the ethyl acetate, the ozonide was gradually added to a mixture of boiling water containing a small amount of hydrochloric acid and zinc dust. The resultant mixture was then subjected to steam distillation. The steam distillate was treated with 2,4-dinitrophenylhydrazine in sulfuric acid. The 2,4-dinitrophenylhydrazone of propionaldehyde (m.p. 154–155° after recrystallization from alcohol) was obtained. A mixture of authentic propionaldehyde 2,4-dinitrophenylhydrazone with this material showed no change in melting point.

The residue from the steam distillation was extracted with ether. After removal of the ether, the ether soluble material was treated with aqueous potassium permanganate and heated. Dilute sulfuric acid was then added to the cool solution. A small amount of sodium bisulfite removed the manganese dioxide precipitate from the slightly acidic solution. Extraction with benzene was followed by an extraction of the benzene extracts with aqueous sodium hydroxide (5%). Acidification of the alkaline solution yielded a solid acid. Purification by recrystallization from benzene and petroleum ether gave a product (m.p. 186–187.5°) which was identical with an authentic specimen of *N*-benzoyl anthranilic acid.

Preparation and pyrolysis of N-2,6-dimethylphenylbenzimidoyl γ,γ-dimethylallyl ether, (VIII). γ,γ-Dimethylallyl bromide, prepared by the addition of hydrogen bromide to isoprene in glacial acetic acid, was converted to γ,γ-dimethylallyl acetate by means of acetic anhydride and fused potassium acetate. Saponification of the acetate gave γ,γ-dimethylallyl alcohol (b.p. 139–141°, lit.[5] 141°). The *N*-phenyl urethane melted at 63.5° (lit.[5] 63.5–64.5°).

2,6-Dimethylaniline was benzoylated and the benzoyl derivative (m.p. 163–164°) was converted to *N*-2,6-dimethylphenylbenzimidoyl chloride by means of thionyl chloride. The addition of *N*-2,6-dimethylphenylbenzimidoyl chloride in benzene to sodium γ,γ-dimethylallyloxide in an atmosphere of nitrogen yielded the desired ether, *N*-2,6-dimethylphenylbenzimidoyl γ,γ-dimethylallyl ether (b.p. 117–129°/0.005–0.03 mm.).

Anal. Calcd. for $C_{20}H_{23}NO$: C, 82.0; H, 7.93. Found: C, 81.9; H, 7.90.

Pyrolysis, either without solvent or dissolved in dimethylaniline yielded *N*-2,6-dimethylphenyl benzamide (m.p. 163–164°) as the only isolable solid product. A substance believed to be isoprene (n_D^{20} 1.4098) was collected in a cold trap.

MINNEAPOLIS 14, MINN.

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(5) W. G. Young and I. D. Webb, *J. Am. Chem. Soc.*, **73**, 781 (1951).