[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

# Ortho Esters, Imidic Esters and Amidines. VIII. Thermal and Acid-catalyzed Rearrangements of Allylic N-Phenylformimidates

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RECEIVED AUGUST 3, 1959

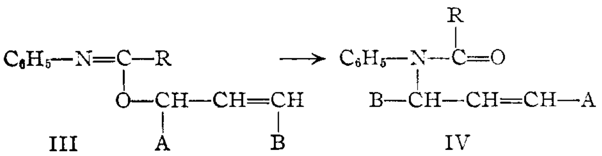
Thermal rearrangement of a number of allylic N-phenylformimidates resulted in high yields of N-allylic formanilides. When the allylic group was unsymmetrically substituted, inversion of the allylic group accompanied its migration. In the presence of catalytic amounts of sulfuric acid, the allylic N-phenylformimidates underwent rapid reaction at lower temperatures. The rearranged products were obtained in lower yields; unsymmetrically substituted esters gave mixtures of allylic isomers. Approximately the same mixture of isomers was obtained from α- and γ-methylallyl N-phenylformimidate. Decomposition into unsubstituted formanilide and 1,3-butadiene accompanied the rearrangement of these esters in the presence of acid. Carbonium ions or ion pairs are probable as intermediates in the acid-catalyzed reactions, whereas the thermal rearrangements must involve pseudo-cyclic transition states.

At high temperatures, aryl N-phenylbenzimidates (Ia) undergo rearrangement to N-arylbenzanilides (IIa) by an intramolecular mechanism.[1,2] The corresponding alkyl esters are much more resistant to thermal rearrangement,[1] but in the presence of strong acids, alkyl N-phenylformimidates (Ib) undergo rearrangement to N-alkylformanilides (IIb) at much lower temperatures by a mechanism which is not strictly intramolecular.[3] Allylic N-phenylbenzimidates (IIIa) undergo thermal rearrangement (210–215°) to N-allylic benzanilides (IVa) by an intramolecular mechanism which must be analogous to the *ortho*-Claisen rearrangement, since the allylic group becomes inverted in the course of the rearrangement.[4]

$$C_6H_5N{=}C(OR){-}R' \longrightarrow C_6H_5N(R){-}C({=}O){-}R'$$

I II

a, R = Ar; R′ = $C_6H_5$
b, R = Me, Et, *i*-Am; R′ = H



$$C_6H_5{-}N{=}C(R){-}O{-}CH(A){-}CH{=}CH(B) \longrightarrow C_6H_5{-}N(CH(B){-}CH{=}CH{-}A){-}C(R){=}O$$

III IV

a, R = $C_6H_5$
b, R = H
A, B = H or $CH_3$

The purpose of the present work was twofold: first, to determine if the easily acquired allylic N-phenylformimidates (IIIb)[5] behave like the corresponding benzimidates on pyrolysis and, secondly, to examine the effect of strong acid on the course of the rearrangement of allylic N-phenylformimidates.

## Experimental[6]

**γ-Methylallyl and β,γ-dimethylallyl alcohols** were prepared by reduction of the corresponding aldehydes with lithium aluminum hydride.[7] **α-Methylallyl alcohol** was prepared from acrolein and methylmagnesium iodide.[8] The **allyl and β-methylallyl alcohols** used were the commercially available products.

**Preparation of Allylic N-Phenylformimidates.**—One mole of ethyl N-phenylformimidate[9] (or, in one expt., methyl N-phenylformimidate[5]) was heated with two moles of the allylic alcohol and the ethyl (or methyl) alcohol was distilled through a 2-ft. glass helices-packed column as it was formed. The excess allylic alcohol and the allylic N-phenylformimidate were then distilled under reduced pressure through the same column. Details on yields and products are given in Table I.

**Thermal Rearrangement of Allylic N-Phenylformimidates.**—The imidic esters were heated in an oil-bath at 220–235° for three hours and the reaction mixtures were then distilled through a 2-ft. glass helices-packed column. Details on yields and products are given in Table II.

**Hydrogenation of N-Allylic Formanilides.**—These compounds were hydrogenated in methanol solution using 5% palladium-on-charcoal catalyst, with initial hydrogen pressures of *ca.* 60 p.s.i. The saturated formanilides were obtained in almost quantitative yields by distillation, after removing the catalyst and solvent. Their physical properties and analytical data are given in Table III.

**Hydrolysis of N-Alkylformanilides.**—The saturated formanilides were hydrolyzed by overnight refluxing with excess 10% hydrochloric acid. After the reaction mixtures were made basic, the N-alkylanilines were extracted into ether, the ether solutions were dried, the solvent was removed and the residues were fractionally distilled under reduced pressure. The following N-alkylanilines were characterized by means of their physical properties, derivatives, and, in the case of the previously unknown N-1,2-dimethylpropylaniline, elementary analysis: **N-*n*-Propylaniline,** b.p. 85° ((6 mm.), $n^{20}\text{D}$ 1.5422, $n^{25}\text{D}$ 1.5402, $d^{25}$ 0.9464; *MR* (sum.) 44.9, (obsd.) 44.8; *p*-toluenesulfonamide, m.p. 56° (reported[4] 56°). **N-Isobutylaniline,** b.p. 79° (3.2 mm.), $n^{20}\text{D}$ 1.5310, $n^{25}\text{D}$ 1.5290, $d^{25}$ 0.9328; *MR* (sum.) 49.5, (obsd.) 49.3; *p*-toluenesulfonamide, m.p. 122° (reported[10] 122–123°); hydrochloride, m.p. 206° ((reported[11] 192°). **N-*sec*-Butylaniline,** b.p. 93° (8 mm.), $n^{20}\text{D}$ 1.5330, $n^{25}\text{D}$ 1.5310; *MR* (sum.) 49.5, (obsd.) 49.3; *p*-toluenesulfonamide, m.p. 78° (reported 77–78°,[4] 76°[12]); hydrochloride m.p. 136° (reported[4] 135–136°). **N-*n*-Butylaniline,** b.p. 92° (3.9 mm.), $n^{20}\text{D}$ 1.5340, $n^{25}\text{D}$ 1.5320, $d^{25}$ 0.9394; *MR* (sum.) 49.5, (obsd.) 49.2; *p*-toluenesulfonamide, m.p. 52° (reported 47°,[4] 54°[11]); hydrochloride, m.p. 115° (reported 115°[4], 114°[11]). **N-1,2-Dimethylpropylaniline,** b.p. 108° (9.5 mm.), 77° (2.3 mm.), $n^{20}\text{D}$ 1.5297, $n^{25}\text{D}$ 1.5280, $d^{25}$ 0.9308; *MR* (sum.) 54.1, (obsd.) 54.0.

*Anal.* Calcd. for $C_{11}H_{17}N$: C, 80.91; H, 10.50. Found: C, 80.30; H, 10.40.

The hydrochloride melted at 130–132°; acid oxalate, m.p. 125°.

**Hydrolysis of N-Allylic Formanilides.**—The unsaturated formanilides were hydrolyzed in the same way as the saturated compounds. The properties of the allylic anilines were: **N-Allylaniline,** b.p. 220°; hydrochloride, m.p. 110° (re-

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[1] A. W. Chapman, *J. Chem. Soc.* 1743 (1927), and preceding papers.

[2] K. B. Wiberg and B. I. Rowland, THIS JOURNAL, **77**, 2205 (1955).

[3] R. M. Roberts and P. J. Vogt, *ibid.*, **78**, 4778 (1956).

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

[5] R. M. Roberts, T. D. Higgins, Jr., and P. R. Noyes, THIS JOURNAL, **77**, 3801 (1955).

[6] Melting points are corrected, boiling points are not.

[7] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[8] R. Delaby, *Ann.*, [9] **19**, 280, 286 (1923).

[9] R. M. Roberts and P. J. Vogt, *Org. Syntheses*, **35**, 65 (1955).

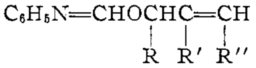
[10] W. J. Hickinbottom, *J. Chem. Soc.*, 992 (1930).

[11] J. von Braun and R. Murjahn. *Ber.*, **59**, 1202 (1926).

[12] G. H. Young, THIS JOURNAL, **56**, 2167 (1934).

TABLE I

ALLYLIC N-PHENYLFORMIMIDATES FROM TRANSESTERIFICATION



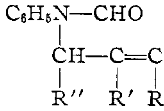
$\mathrm{C_6H_5N{=}CHO\underset{R}{CH}\underset{R'}{C}{=}\underset{R''}{CH}}$

| R | R′ | R″ | Yield, % | B.p., °C. | B.p., Mm. | $n^t_D$ | t, °C. | $d^{25}$ | MR Sum.[a] | MR Obsd. | Empirical formula | Analyses, %[b] Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | 92 | 91 | 5.0 | 1.5325 | 20 | 1.004 | 48.9 | 49.8 | $C_{10}H_{11}NO$ | 74.49 | 74.61 | 6.88 | 6.92 |
| | | | | | | 1.5310 | 25 | | | | | | | | |
| H | Me | H | 78 | 100 | 4.5 | 1.5275 | 20 | 0.9965 | 53.5 | 54.0 | $C_{11}H_{13}NO$ | 75.38 | 75.80 | 7.48 | 7.85 |
| | | | | | | 1.5255 | 25 | | | | | | | | |
| H | H | Me | 71 | 107 | 4.7 | 1.5310 | 20 | 0.9960 | 53.5 | 54.3 | $C_{11}H_{13}NO$ | 75.38 | 74.82 | 7.48 | 7.86 |
| | | | | | | 1.5290 | 25 | | | | | | | | |
| Me | H | H[c] | 71 | 70 | 2.0 | 1.5253 | 20 | 0.9933 | 53.5 | 53.6 | $C_{11}H_{13}NO$ | 75.38 | 75.03 | 7.48 | 7.46 |
| | | | | 95 | 5.4 | 1.5231 | 25 | | | | | | | | |
| H | Me | Me | 83 | 115 | 4.2 | 1.5352 | 20 | 1.007 | 58.1 | 58.3 | $C_{12}H_{15}NO$ | 76.14 | 76.06 | 8.00 | 7.97 |
| | | | | | | 1.5335 | 25 | | | | | | | | |

[a] From summation of atomic refraction values. [b] Analyses by Drs. G. Weiler and F. B. Strauss, Oxford, England. [c] Methyl N-phenylformimidate was used as starting material in this preparation.

TABLE II

N-ALLYLICFORMANILIDES FROM THERMAL REARRANGEMENT OF ALLYLIC N-PHENYLFORMIMIDATES



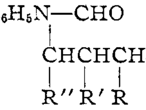
$\mathrm{C_6H_5N(CHO)\text{—}\underset{R''}{CH}\text{—}\underset{R'}{C}{=}\underset{R}{CH}}$

| R″ | R′ | R | Yield, % | B.p., °C. | B.p., Mm. | $n^t_D$ | t, °C. | $d^{25}$ | MR Sum.[a] | MR Obsd. | Empirical formula | Analyses, %[b] Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | 100 | 136 | 10 | 1.5520 | 20 | 1.068 | 48.1 | 48.2 | $C_{10}H_{11}NO$ | 74.49 | 74.74[c] | 6.88 | 6.97[c] |
| | | | | | | 1.5505 | 25 | | | | | | | | |
| H | Me | H | 93 | 98 | 1.3 | 1.5484 | 20 | 1.049 | 52.7 | 52.8 | $C_{11}H_{13}NO$ | 75.38 | 75.45 | 7.48 | 7.62 |
| | | | | | | 1.5464 | 25 | | | | | | | | |
| Me | H | H | 96 | 105 | 1.5 | 1.5380 | 20 | 1.016 | 52.7 | 53.7 | $C_{11}H_{13}NO$ | 75.38 | 75.31 | 7.48 | 7.45 |
| | | | | | | 1.5360 | 25 | | | | | | | | |
| H | H | Me | 85 | 138 | 6.0 | 1.5478 | 20 | 1.050 | 52.7 | 52.8 | $C_{11}H_{13}NO$ | 75.38 | 75.32 | 7.48 | 7.64 |
| | | | | 119 | 2.7 | 1.5460 | 25 | | | | | | | | |
| Me | Me | H | 89 | 100 | 1.3 | 1.5390 | 20 | 1.037 | 57.3 | 57.0 | $C_{12}H_{15}NO$ | 76.14 | 76.40 | 8.00 | 8.08 |
| | | | | | | 1.5370 | 25 | | | | | | | | |

[a] From summation of atomic refraction values. [b] Analyses by Dr. G. Weiler and F. B. Strauss, Oxford, England. [c] The sample analyzed was one from an acid-catalyzed rearrangement.

TABLE III

N-ALKYLFORMANILIDES FROM HYDROGENATION OF N-ALLYLICFORMANILIDES



$\mathrm{C_6H_5N(CHO)\text{—}\underset{R''}{CH}\underset{R'}{CH}\underset{R}{CH_2}}$

| R″ | R′ | R | B.p., °C. | B.p., Mm. | $n^t_D$ | t, °C. | $d^{25}$ | MR Sum.[a] | MR Obsd. | Empirical formula | Analyses, %[b] Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | 124 | 4.8 | 1.5349 | 20 | 1.029 | 48.6 | 49.2 | $C_{10}H_{13}NO$ | 73.58 | 73.59[c] | 8.03 | 8.04[c] |
| | | | | | 1.5332 | 25 | | | | | | | | |
| H | Me | H | 120 | 4.5 | 1.5252 | 20 | 1.017 | 53.2 | 53.2 | $C_{11}H_{15}NO$ | 74.53 | 74.49 | 8.53 | 8.48 |
| | | | | | 1.5232 | 25 | | | | | | | | |
| Me | H | H | 129 | 8.3 | 1.5235 | 20 | 1.018 | 53.2 | 53.8 | $C_{11}H_{15}NO$ | 74.53 | 74.97 | 8.53 | 8.54 |
| | | | | | 1.5215 | 25 | | | | | | | | |
| H | H | Me | 129 | 4.8 | 1.5293 | 20 | 1.015 | 53.2 | 53.7 | $C_{11}H_{15}NO$ | 74.53 | 74.68 | 8.53 | 8.54 |
| | | | | | 1.5273 | 25 | | | | | | | | |
| Me | Me | H | 119 | 3.1 | 1.5255 | 20 | 1.014 | 57.8 | 57.7 | $C_{12}H_{17}NO$ | 75.34 | 75.74 | 8.96 | 8.67 |
| | | | | | 1.5240 | 25 | | | | | | | | |

[a] From summation of atomic refraction values. [b] Analyses by Drs. G. Weiler and F. B. Strauss, Oxford, England. [c] The sample analyzed was prepared by A. Merijan.

ported[13] 110°); acid oxalate, m.p. 119° (reported[13] 120°). **N-β-Methylallylaniline**, b.p. 90° (3 mm.), $n^{20}D$ 1.5550, $n^{25}D$ 1.5530, $d^{25}$ 0.9629; *MR* (sum.) 49.0, (obsd.) 48.9.

*Anal.* Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.60; H, 8.81. The hydrochloride melted at 156°. **N-α-Methylallylaniline**, b.p. 130° (20 mm.), $n^{20}D$ 1.5560, $n^{25}D$ 1.5545, $d^{25}$ 0.9731; *MR* (sum.) 49.0, (obsd.) 48.6.

*Anal.* Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.22; H, 9.02.

The hydrochloride melted at 150°. **N-γ-Methylallylaniline**, b.p. 96° (3 mm.), $n^{20}D$ 1.5580, $n^{25}D$ 1.5565, $d^{25}$ 0.9702; *MR* (sum.) 49.0, (obsd.) 48.8 (reported[13] $n^{20}D$ 1.5587, $d^{20}$ 0.9613).

*Anal.* Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.69; H, 8.90.

**Acid-catalyzed Rearrangement of Allylic N-Phenylformimidates. Allyl N-Phenylformimidate.**—A mixture of 32 g.

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[13] F. B. Dains, R. Q. Brewster, J. S. Blair and W. C. Thompson, THIS JOURNAL, 44, 2637 (1922).

(0.20 mole) of allyl N-phenylformimidate and 0.874 g. (0.0086 mole) of concentrated sulfuric acid was heated in an oil-bath. As soon as the inside temperature reached 115°, a vigorous reaction occurred and the inside temperature rose rapidly to 164° (oil-bath only 130°). Heating was stopped immediately and the mixture was allowed to cool slowly to room temperature. Distillation under reduced pressure gave 1 g. of the unchanged ester, b.p. 100° (7.5 mm.), and 22.5 g. (70%) of N-allylformanilide, b.p. 136° (10 mm.). Physical constants and analyses are given in Table II. A dark liquid residue was left. The N-allylformanilide was hydrolyzed to N-allylaniline (see above).

**β-Methylallyl N-Phenylformimidate.**—A mixture of 46 g. (0.263 mole) of β-methylallyl N-phenylformimidate and 10.3 g. (0.010 mole) of concentrated sulfuric acid was heated in the same apparatus as above. When the temperature of the reaction mixture reached 107°, a vigorous boiling occurred and the temperature rose rapidly to 154°. Heating was stopped and the mixture was allowed to cool to about 60°. Distillation yielded 30.4 g. (65%) of N-β-methylallylformanilide, the physical constants of which were identical with those of the product from thermal rearrangement.

The N-β-methylallylformanilide was catalytically reduced to N-isobutylformanilide and this was hydrolyzed to N-isobutylaniline. The physical properties of these compounds were identical with those of the products obtained from thermal rearrangements; the *p*-toluenesulfonamide (m.p. 122°) and the hydrochloride (m.p. 206°) of the amine were prepared.

**γ-Methylallyl N-Phenylformimidate.**—A mixture of 47.5 g. (0.270 mole) of γ-methylallyl N-phenylformimidate and 1.01 g. (0.0099 mole) of concentrated sulfuric acid was heated. A gas trap immersed in an acetone–Dry Ice mixture was provided. When the temperature of the reaction mixture reached 98°, a vigorous boiling occurred and the temperature rose rapidly to 140°. Heating was stopped immediately and the flask was allowed to cool to about 60°.

The contents of the acetone–Dry Ice trap were treated with bromine; 1.20 g. of 1,2,3,4-tetrabromobutane, m.p. 118–119° (reported[14] 118–119°), was obtained.

The reaction mixture was distilled under reduced pressure, the fraction boiling at 127–137° (6.5 mm.) being collected. This amounted to 30 g. (63%) of the theoretical amount of rearranged products.

This 30 g. of material was catalytically reduced, the reduced products were hydrolyzed and the hydrolysis products were distilled through a 2-ft. glass helices-packed column. The following fractions were collected: (a) 6 g., b.p. 35° (1.4 mm.); (b) 3 g., b.p. 64° (1.4 mm.); and (c) 10 g., b.p. 74° (1.4 mm.). Fraction a was redistilled and identified as aniline by its physical constants ($n^{20}$D 1.5861) and its benzenesulfonyl derivative, m.p. 112° (reported[15] 110°). Fraction b was identified as N-*sec*-butylaniline through its hydrochloride, m.p. 136°, and its *p*-toluenesulfonamide, m.p. 77°. Fraction c was identified as N-*n*-butylaniline through its hydrochloride, m.p. 115°, and its *p*-toluenesulfonamide, m.p. 52°.

**α-Methylallyl N-Phenylformimidate.**—A mixture of 32 g. (0.183 mole) of α-methylallyl N-phenylformimidate and 0.71 g. (0.0070 mole) of concentrated sulfuric acid was treated as above. The exothermic reaction occurred when the temperature of the reaction mixture reached 80°, and the temperature rose rapidly to 125°.

The contents of the cold trap were treated with bromine; 1,2,3,4-tetrabromobutane, m.p. 118° (after recrystallization from ligroin), was obtained in 21% yield.

The reaction mixture, upon distillation as before, gave 23.5 g. (74%) of products boiling at 127–144° (5.4 mm.). This entire amount was catalytically reduced, hydrolyzed and distilled as before, yielding the fractions: (a) 5.6 g., b.p. 45° (2.2 mm.); (b) 1.5 g., b.p. 65° (2.2 mm.); and (c) 6.0 g., b.p. 84° (2.5 mm.). These fractions were identified through the same derivatives as before as (a) aniline, (b) N-*sec*-butylaniline and (c) N-*n*-butylaniline.

**β,γ-Dimethylallyl N-Phenylformimidate.**—A mixture of 50 g. (0.265 mole) of β,γ-dimethylallyl N-phenylformimidate and 1.0 g. (0.0098 mole) of concentrated sulfuric acid was treated as before. The exothermic reaction occurred when the temperature of the reaction mixture reached 87°, and the temperature rose rapidly to 120°.

The material collected in the cold trap (3.5 g.) was isoprene, b.p. 35° (reported[16] 34.5°), $n^{20}$D 1.4216 (reported[16] 1.4221). The Diels–Alder adduct was prepared from 2 g. of it and 2 g. of powdered maleic anhydride. Recrystallized from ligroin, the 4-methyl-$\Delta^4$-tetrahydrophthalic anhydride melted at 63° (reported[17] 63–64°).

The reaction mixture, upon distillation as before, gave 33 g. (66%) of products boiling at 141–153° (8.5 mm.). This entire amount was catalytically reduced, hydrolyzed and distilled as before, yielding the fractions: (a) 4.7 g., b.p. 42° (1.6 mm.); (b) 2.0 g., b.p. 80° (2.6 mm.); and (c) 10 g., b.p. 94° (2.6 mm.). On the basis of b.p., (a) was aniline and (b) was N-1,2-dimethylpropylaniline. Fraction c had $n^{20}$D 1.5268, $n^{25}$D 1.5250; *MR* (sum.) 54.1, (obsd.) 53.9. It was assumed to be N-2-methylbutylaniline.

*Anal.* Calcd. for $C_{11}H_{17}N$: C, 80.91; H, 10.50. Found: C, 80.91; H, 10.46.

The *p*-toluenesulfonamide melted at 85°; acid oxalate, m.p. 148°.

## Discussion of Results

The allylic N-phenylformimidates listed in Table I were prepared by transesterification of ethyl or methyl N-phenylformimidate with the appropriate allylic alcohol.[5] When heated at about 220–235° for three hours, the imidic esters underwent smooth and almost complete rearrangement to N-allylic formanilides (Table II). In the cases of the esters in which the allylic group was unsymmetrically substituted, it was found that inversion of the allylic group accompanied its migration from oxygen to nitrogen, as was true with the corresponding benzimidates.[4] The structures of the N-allylic formanilides were proved by catalytic hydrogenation to the saturated formanilides (Table III), followed by hydrolysis of these to the N-alkylanilines. Some of the N-allylic formanilides were also hydrolyzed directly to N-allylic anilines.

When a small amount of concentrated sulfuric acid (the same proportion used with the alkyl N-phenylformimidates[3]) was added to the allylic N-phenylformimidates before heating, it was found that a strongly exothermic reaction took place at temperatures between 80–115°, and rearrangement took place rapidly without further application of heat. In the cases of allyl and β-methylallyl N-phenylformimidates, the same rearranged products were obtained as from the thermally induced reactions, but the yields were about 30% lower. (The high-boiling by-products in the distillation residues were not investigated.) In the cases of the esters with unsymmetrically substituted allylic groups, instead of obtaining a high yield of the pure formanilide having the inverted allylic group, a mixture of formanilides was produced from each acid-catalyzed rearrangement. These mixtures consisted of the isomers of the N-allylic formanilides and, in addition, unsubstituted formanilide. The presence of the unsubstituted formanilide complicated the separation of the products, because, although the unsubstituted formanilide is of lower molecular weight, by virtue of hydrogen bonding it has a boiling point of the same order of magnitude as the higher molecular weight substituted formanilides. Hence, no attempt was made to isolate these formanilides from their mixtures, but they were directly hydrogenated and the saturated amides were hydrolyzed. It was then easy to separate aniline

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(14) G. Ciamician and P. Magnaghi, *Ber.*, **19**, 570 (1886).

(15) A. Ginsberg, *ibid.*, **36**, 2706 (1903).

(16) S. V. Lebedev and A. O. Yakybchik, *J. Chem. Soc.*, 823 (1928).

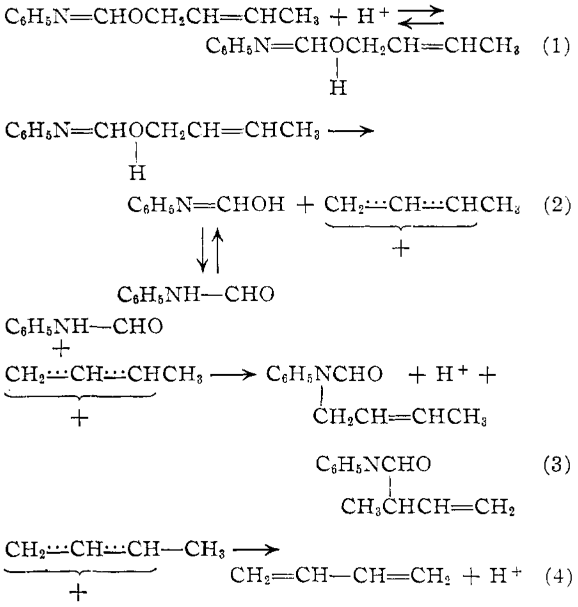
(17) O. Diels and K. Alder, *Ber.*, **470**, 102 (1929).

and the higher boiling isomeric N-substituted anilines by fractional distillation. In these reactions in which unsubstituted formanilide was produced, significant amounts of volatile products were evolved during the exothermic reaction. These were collected in a cold trap and were found to be 1,3-butadiene, from α- and γ-methylallyl esters, and isoprene, from β,γ-dimethylallyl ester.

Mixtures containing approximately the same proportion of isomeric N-α-methylallylformanilide and N-γ-methylallylformanilide were produced from both α-methylallyl N-phenylformimidate and γ-methylallyl N-phenylformimidate, with the primary allylic isomer predominating in a ratio of about 4:1. The mixture of isomers obtained by acid-catalyzed rearrangement of β,γ-dimethylallyl N-phenylformimidate also apparently contained the primary allylic isomer in predominant amount, but the characterization of this mixture was not rigorous.

**Mechanisms of the Thermal and Acid-catalyzed Rearrangements.**—The mechanism of the thermal rearrangement of the allylic N-phenylformimidates is obviously the same as that of the benzimidates, which was described by Mumm and Möller[4] as involving a pseudo-cyclic transition state analogous to that of the *ortho*-Claisen rearrangement. The rearrangement is practically free of side reactions, like that of the aryl N-phenylbenzimidates, but takes place at a much lower temperature. This probably reflects the lower energy of a transition state with a six-membered ring compared to a four-membered ring.[2]

The observed differences in the rearrangements of the allylic N-phenylformimidates produced by the addition of sulfuric acid; *e.g.*, (1) more rapid and exothermic reaction at lower temperatures, (2) production of mixtures of allylic isomers and (3) decomposition into diene and formanilide, are all inconsistent with an intramolecular mechanism and suggestive of carbonium ion or ion-pair intermediates. A mechanism which appears to be reasonable for the reactions in the presence of acid is outlined, using γ-methylallyl N-phenylformimidate as an example.



$$C_6H_5N{=}CHOCH_2CH{=}CHCH_3 + H^+ \rightleftarrows C_6H_5N{=}CH\underset{\substack{|\\ H}}{O}CH_2CH{=}CHCH_3 \qquad (1)$$

$$C_6H_5N{=}CH\underset{\substack{|\\ H}}{O}CH_2CH{=}CHCH_3 \longrightarrow \underset{\substack{\downarrow\uparrow\\ C_6H_5NH{-}CHO}}{C_6H_5N{=}CHOH} + \underbrace{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_3}_{+} \qquad (2)$$

$$C_6H_5NH{-}CHO + \underbrace{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CHCH_3}_{+} \longrightarrow C_6H_5\underset{\substack{|\\ CH_2CH{=}CHCH_3}}{N}CHO + H^+ + C_6H_5\underset{\substack{|\\ CH_3CHCH{=}CH_2}}{N}CHO \qquad (3)$$

$$\underbrace{CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH}_{+}{-}CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H^+ \qquad (4)$$

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[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

# Polymerization of Ethylene with Bis-(cyclopentadienyl)-titanium Dichloride and Diethylaluminum Chloride

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RECEIVED AUGUST 31, 1959

The reaction which takes place between bis-(cyclopentadienyl)-titanium dichloride (I) and diethylaluminum chloride has been examined. Spectroscopic evidence has been obtained for the existence of three complexes: $(C_5H_5)_2TiCl_2{\cdot}(C_2H_5)_2AlCl$ (II), $(C_5H_5)_2C_2H_5TiCl{\cdot}C_2H_5AlCl_2$ (III) and $(C_5H_5)_2TiCl{\cdot}C_2H_5AlCl_2$ (IV). A correlation of spectral changes with catalytic activity has indicated that complex III, or some species readily derived from it, is the active catalyst for the polymerization of ethylene.

## Introduction

Bis-(cyclopentadienyl)-titanium dichloride, $(C_5H_5)_2TiCl_2$ (I), reacts with alkylaluminum compounds to form soluble catalysts for the low temperature, low pressure polymerization of ethylene.[1-3] Previous reports have described the systems derived from dimethylaluminum chloride[4] and from methylaluminum dichloride.[5] The present paper is concerned with a more detailed study of the diethylaluminum chloride system. From a mechanistic point of view this appears to be the most important system, inasmuch as the reaction of the "sandwich" dichloride (I) with diethylaluminum chloride appears to be essentially independent of the presence of ethylene. The methylaluminum systems, on the other hand, undergo quite different reactions in the absence of monomer, but appear to parallel the diethylaluminum chloride system in the presence of ethylene. Although the Ziegler polymerization of ethylene with heterogeneous catalysts may differ in some details from the polymerization with these soluble catalysts, it is believed that the fundamental mechanism is the same.

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(1) D. S. Breslow, U. S. Patent 2,827,446 (1958).

(2) D. S. Breslow and N. R. Newburg, THIS JOURNAL, **79**, 5072 (1957).

(3) D. S. Breslow and N. R. Newburg, *ibid.*, **81**, 81 (1959).

(4) J. C. W. Chien, *ibid.*, **81**, 86 (1959).

(5) W. P. Long, *ibid.*, **81**, 5312 (1959).