reaction varied from 2.8 to 3.5 amp. and the voltage remained at 19 to 20 V. The reaction was carried out in an ice-water cooled three-neck flask, equipped with a condenser leading to a Dry Ice trap, a Tru-Bore stirrer, and the electrodes. To the flask was added 30 g. of (+)-2-methylbutanoic acid and 9 g. of KOH dissolved in 30 ml. of water. After 193 minutes of current passage another 20 g. of (+)-2-methylbutanoic acid was added and electrolysis was continued for 145 minutes; total 67,000 coulombs or 0.64 Faraday. The light yellow upper layer after separation and drying (sodium sulfate) weighed 11.0 g. One gram of residue was obtained when the 9 g. of liquid in the Dry Ice trap was permitted to warm up to room temperature. The combined fractions were distilled twice, the second time through a small Podbielniak column, and the following principal fractions were obtained:

1. b.p. 96.6–98.0°; 1.09 g.; n_D^{25} 1.3977; α_D^{27} 0.00° (l, 0.5, neat)
2. b.p. 151.0–161.5°; 1.51 g.; n_D^{25} 1.4036; α_D^{27} 5.44° (l, 0.5, neat)
3. b.p. 161.5–162.1°; 1.25 g.; n_D^{25} 1.4031; α_D^{27} 6.31° (*l*, 0.5, neat)

The α-naphthylurethan of fraction 1, after one crystallization from cyclohexane, had m.p. 95.5–96°, undepressed by admixture of the α-naphthylurethan of authentic (±)-2-butanol. Fractions 2 and 3 analyzed for slightly impure butyl methylbutanoate.

Anal. Calc'd for $C_9H_{18}O_2$: C, 68.3; H, 11.4. Found (fraction 2): C, 69.3; H, 11.8. Found (fraction 3): C, 70.5; H, 11.1.

Fractions 2 and 3 were combined and saponified according to the method of Kharasch, *et al.*,[9] by using aqueous KOH in diethylene glycol and heating at 155° for one hour. The reaction mixture was steam-distilled directly. The distillate on thorough drying with sodium sulfate had n_D^{25} 1.3953 and α_D^{28} 0.00° (*l*, 0.5, neat). The α-naphthylurethan had m.p. 95–96° and did not depress the melting point of the α-naphthylurethan of authentic (±)-2-butanol. Acidification of the residue and steam-distillation gave crude (+)-2-methylbutanoic acid with a rotation of α_D^{27} 5.0° (*l*, 0.5, neat).

From the aqueous phase of the electrolysis mixture it was possible to recover 4.4 g. of unchanged (+)-2-methylbutanoic acid, b.p. 93–95° (38 mm.), α_D^{27} 8.91° (*l*, 0.5, neat).

(±)-2-Butyl ester of (+)-2-methylbutanoic acid. A mixture of 5.1 g. of (+)-2-methylbutanoic acid, 44 g. of (±)-2-butanol, and 1.0 g. of sulfuric acid was refluxed for 41 hours. Distillation after workup afforded a 57% yield of ester, b.p. 160–163°. Redistillation through a small Podbielniak column afforded a middle cut with n_D^{25} 1.4035 and α_D^{27} +6.60° (*l*, 0.5, neat).

WM. H. NICHOLS CHEMICAL LABORATORY
NEW YORK UNIVERSITY
NEW YORK 53, N. Y.

---

(12) F. C. Whitmore and J. H. Olewine, *J. Am. Chem. Soc.*, 60, 2569 (1938).

The Boron Fluoride Catalyzed Condensation of Pyridine-2-Aldehyde[1]

C. S. MARVEL AND J. K. STILLE

Received June 18, 1956

In an attempt to prepare 2-pyridalacetone by the condensation of pyridine-2-aldehyde and acetone in the presence of boron trifluoride we found that the reaction product was composed of 2-pyridoin and 2-pyridil. The same products were obtained from pyridine-2-aldehyde without the addition of acetone. Hensel[2] has shown that 2-pyridoin can be obtained by the action of acetic acid on pyridine-2-aldehyde. The infrared spectrum of his 2-pyridoin showed weak bands at 1700 and 1710 cm.$^{-1}$ which indicates that he too had obtained some 2-pyridil. Apparently boron fluoride serves as a benzoin reaction catalyst with pyridine-2-aldehyde. The 2-pyridil probably is formed by air oxidation of the pyridoin although the amount of this product formed in the reaction was not increased by passing air through the reaction mixture.

No similar condensation of pyridine-3-aldehyde or pyridine-4-aldehyde with boron fluoride was obtained.

EXPERIMENTAL

In a 500-ml. three-necked round-bottomed flask equipped with a mercury sealed stirrer, a delivery tube, and a drying outlet tube, was added 44 g. (0.4 mole) of freshly distilled pyridine-2-aldehyde. The aldehyde was chilled and saturated with BF_3 by the method of Breslow and Hauser.[3] The red color which quickly formed, turned dark red, and the mixture thickened to a syrupy consistency. The saturation was usually complete after two hours. At the end of this period, the mixture was allowed to come to room temperature and to it was added 46.4 g. of acetone. The reaction mixture retained the deep red color, and upon the addition of an aqueous sodium acetate solution, a bright orange precipitate formed which was removed by filtration, (14.6 g., 34.1%). The same product was obtained with the omission of the acetone, and the yield was not dependent on the sodium acetate solution for hydrolysis, as an aqueous sodium carbonate solution served as well. The product could be recrystallized from alcohol-water or cyclohexane. The final purification step consisted of crystallization from water by dissolving the product in a slightly acidic solution at 90°, and neutralization with base. M.p. 153° (lit. 156°).[2]

Anal. Calc'd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.29; H, 4.78; N, 12.93.

The structure was consistent with that described by other investigators[4,5] and showed infrared bands previously reported.[2,6] However, the broad band from the highly bonded alcohol appeared at 2670 cm.$^{-1}$ Characteristic absorption maxima at 1592 and 1275 cm.$^{-1}$ were also observed.

The filtrate from the 2-pyridoin was extracted with ethyl ether until the extracts no longer contained a yellow coloration. The extracts were combined, dried over magnesium sulfate, and the ether was stripped under reduced pressure. The product was recrystallized from absolute ethanol, yielding 3 g. (7.1%) of light lemon-yellow crystals (m.p. 154°). This material gave double 1,2-dicarbonyl peaks at 1700 and 1710 cm.$^{-1}$, which were present in Hensel's spectrum.[2,3]

Anal. Calc'd for $C_{12}H_8N_2O_2$: C, 67.91; H, 3.80; N, 13.20. Found: C, 67.69; H, 4.07; N, 13.10.

---

(1) The work discussed herein was performed as a part of the synthetic rubber research project sponsored by the National Science Foundation.

(2) H. Hensel, *Angew. Chem.*, 65, 491 (1953).

(3) D. S. Breslow and C. R. Hauser, *J. Am. Chem. Soc.*, 62, 2385 (1940).

(4) F. Cramer and W. Krum, *Ber.*, 86, 1586 (1953).

(5) F. Cramer, *Angew Chem.*, 65, 212 (1953).

(6) W. Lüttke and H. Marsen, *Z. Elektrochem.*, 57, 680 (1953).

The infrared spectra of the products were run on a Perkin-Elmer model 21 spectrophotometer.

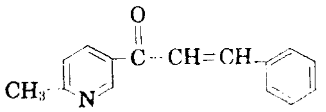
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Reactivity Ratios of 2-Methyl-5-cinnamoylpyridine, 3-Cinnamoylpyridine, and 3-Pyridalacetophenone with Styrene

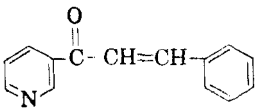
C. S. MARVEL, VERONIKA SZIRAKY, AND JAMES ECONOMY

Received June 18, 1956

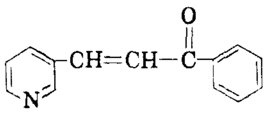
To find the effect of structure on the reactivity of three similar monomers, the reactivity ratios of 2-methyl-5-cinnamoylpyridine (I), 3-cinnamoylpyridine (II), and 3-pyridalacetophenone (III) with styrene were determined as suggested by Mayo and Lewis.[1] Polymerization was achieved in benzene solution and the composition of the resulting polymers was determined by nitrogen analysis. The results are summarized in Table I. The error in the "r" values was estimated by assuming a 0.1 per cent error in the nitrogen analysis.



I



II



III

TABLE I

REACTIVITY RATIOS

M_1	r_1	M_2	r_2
Styrene	0.92 ± 0.08	2-Methyl-5-cinnamoylpyridine	−0.15 ± 0.2
Styrene	0.85 ± 0.05	3-Cinnamoylpyridine	0.09 ± 0.1
Styrene	0.50 ± 0.1	3-Pyridalacetophenone	0.00 ± 0.25

The very low "r" values of these ketones are in agreement with previous experience[2] that pyridine analogs of chalcone do not homopolymerize. It is of interest that the r_1 values of styrene vary from about 1.0 to 0.5. Since the reactivity ratio is a measure of the tendency of one monomer to add to itself or to the comonomer, the results show that the styrene radical is less reactive toward 2-methyl-5-cinnamoylpyridine and 3-cinnamoylpyridine than toward 3-pyridalacetophenone. This seems to indicate that a double bond adjacent to the pyridine ring is more active than one next to the benzene ring.

We were unsuccessful in attempts to determine reactivity ratios with butadiene because of failure to achieve copolymerization in a bulk recipe.

EXPERIMENTAL

3-Pyridalacetophenone. The method described before[2] was followed using one-molar quantities. There was obtained 50 g. of 3-pyridalacetophenone, m.p. 102–103°.

2-Methyl-5-cinnamoylpyridine. The synthesis of 2-methyl-5-cinnamoylpyridine[2] was improved. The compound was prepared by adding 44 g. (0.41 mole) of redistilled benzaldehyde to a pre-cooled solution of 18 g. of sodium hydroxide in 165 ml. of water and 50 ml. of methanol. Then 55 g. (0.41 mole) of redistilled 2-methyl-5-acetylpyridine was added slowly keeping the temperature below 5°. After three hours of stirring below 15° the mother liquor was decanted and the yellow oil was dissolved in 1500 ml. of 10% by volume sulfuric acid. This solution was heated on the steam-bath for one hour, diluted with 4000 ml. of water, cooled, and carefully neutralized with a 10% solution of sodium hydroxide until a heavy precipitate was formed. The solid was collected, and the filtrate was treated twice more in the same manner. After drying, the crude product was recrystallized twice from cyclohexane yielding 40.3 g. (47%) of a light green crystalline solid, m.p. 79°.

3-Cinnamoylpyridine. This ketone was prepared by adding 20.6 g. (0.2 mole) of redistilled benzaldehyde and 23.6 g. (0.2 mole) of redistilled 3-acetylpyridine to a solution of 2.5 ml. of piperidine in 250 ml. of pyridine. The mixture was heated on the steam-bath for one hour and for an additional 15 minutes under reflux. It was poured into 1500 ml. of cold water and left standing overnight. Dehydration with sulfuric acid (225 ml. in 850 ml. of water) and neutralization were carried out as reported above for 2-methyl-5-cinnamoylpyridine. After drying, the resulting crude product was recrystallized twice from cyclohexane yielding 9.3 g. (22.3%) of a light yellow crystalline product, m.p. 84.5–85°.

The molecular weight of the product was determined by the Rast method.[3]

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.38; H, 5.26; N, 6.98; M.W., 209. Found: C, 80.46; H, 5.42; N, 6.71; M.W., 204.

The infrared absorption spectrum showed characteristic bands at 1665, 1645, 1610, 1607, 1500, 985, and 695 cm.$^{-1}$ in agreement with the proposed structure.*

The ultraviolet absorption spectrum showed maxima at 240 mμ, log ε 6.38, and at 312 mμ, log ε 6.49.**

Reactivity ratio determinations. Polymerization was carried out in benzene solution at 50° using 0.4000 g. of azobisisobutyronitrile initiator. The polymer was precipitated in low-boiling petroleum ether and unreacted monomer was extracted by the same solvent in a Soxhlet extractor for four hours. For further purification the polymer was twice reprecipitated from benzene. The conversions in these reactivity ratio studies were of the order of 5 to 10% and never more than 10%. The experimental data are summarized in Table II.

---

(1) Mayo and Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

(2) Marvel, Coleman, and Scott, *J. Org. Chem.*, **20**, 1785 (1955).

(3) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 3rd edition, John Wiley and Sons, Inc., New York, 1947, p. 50.

* Mr. J. Brader determined the infrared spectrum and made the interpretation.

** The ultraviolet analysis was determined by Miss G. Meerman.