[Contribution from the Noyes Chemical Laboratory, University of Illinois]

PYRIDINE ANALOGS OF CHALCONE AND THEIR POLYMERIZATION REACTIONS

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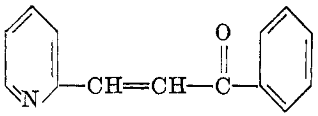
In the past few years the polymerization reactions of chalcone, its substituted derivatives, and the furan and thiophene analogs have been studied in this laboratory (1–4). The present investigation deals with the preparation and polymerization reactions of the pyridine analogs of chalcone and cinnamic acid.

With the exception of 2-cinnamoylpyridine (6), the pyridine analogs of chalcone have not been prepared. The first attempts to prepare 2-pyridalacetophenone (I) from 2-pyridine aldehyde and acetophenone by the method described for benzalacetophenone (5) resulted in an oily mixture of the desired ketone, the Michael-type addition product (II) of 2-pyridalacetophenone and acetophenone, and the aldol (III). When excess alcohol was used the Michael addition product could be isolated whereas with no alcohol (6) the aldol was the only product isolated. Therefore the procedure was altered in subsequent reactions by lowering the temperature and changing the solvent to methanol. This modification eliminated oil formation. The Michael addition reaction was eliminated by charging the aldehyde at once and then adding the acetophenone dropwise or in small portions over a period of 30 minutes to an hour.



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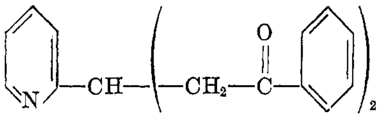

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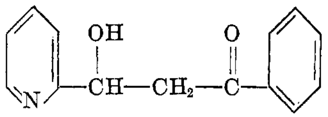
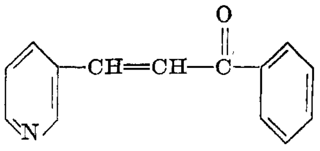


III

These modifications were used in the preparation of 3-pyridalacetophenone (IV), 2-cinnamoylpyridine (V), 4-cinnamoylpyridine (VI), 2-methyl-5-cinnamoylpyridine (VII), and 2-pyridal-2′-acetylpyridine (VIII); and only the α,β-unsaturated ketones were isolated.



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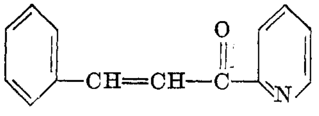

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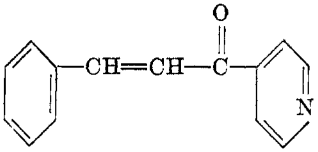

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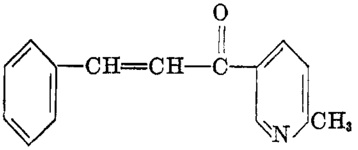

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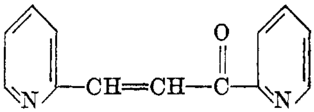
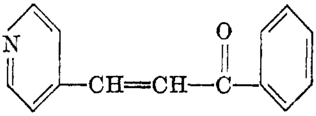
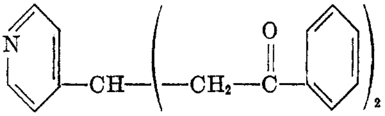


VIII

In the first attempt to prepare 4-pyridalacetophenone (IX), (by the same procedure as described for benzalacetophenone), only the Michael addition product (X) was isolated. In additional runs, the temperature was lowered and the solvent was changed resulting in a mixture of 4-pyridalacetophenone and about 10 per cent Michael addition product which could only be separated by distillation at reduced pressure.

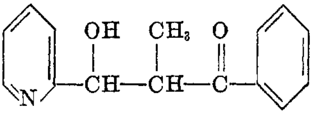


IX



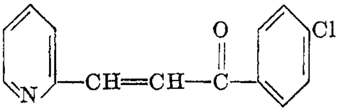
X

An attempt to condense 2-pyridine aldehyde and propiophenone gave the aldol (XI) as the only product. This compound is very stable and attempts to dehydrate it have been unsuccessful.

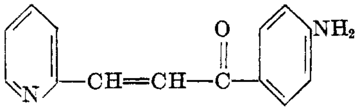


XI

The preparation of 2-pyridal-*p*-chloroacetophenone (XII) and 2-pyridal-*p*-aminoacetophenone (XIII) offered no difficulty either with side reactions or purification.



XII



XIII

β-(3-Pyridyl)acrylic acid (XIV), prepared from 3-pyridine aldehyde and malonic acid, has been described in the literature (7, 8) as a brown solid which contained a trace impurity that can be removed (9) to give a white solid. The white solid was used in our polymerization studies. β-(2-Pyridyl)acrylic acid

(XV) and β-(4-pyridyl)acrylic acid (XVI) were prepared and purified by the same method used for the 3-isomer.

R—CH=CH—CO_2H
XIV. R = *3*-pyridyl
XV. R = *2*-pyridyl
XVI. R = *4*-pyridyl

2-Pyridalacetophenone, 2-pyridal-*p*-chloroacetophenone, 3-pyridalacetophenone, 4-pyridalacetophenone, 2-cinnamoylpyridine, 2-methyl-5-cinnamoylpyridine, 4-cinnamoylpyridine, and 2-pyridal-2′-acetylpyridine formed copolymers with acrylonitrile; and all except 2-cinnamoylpyridine and 2-pyridal-2′-acetylpyridine gave copolymers with isoprene, methyl acrylate, methyl methacrylate, and styrene in free radical-initiated systems. None of these compounds formed polymers with isobutyl vinyl ether, maleic anhydride, trichloroethylene, vinyl acetate, vinyl chloride, or 2-vinylpyridine in free radical-initiated systems.

No copolymers were obtained with the β-pyridylacrylic acids and methyl acrylate, methyl methacrylate, styrene, and vinyl acetate. These acids did give copolymers with acrylonitrile.

All of the copolymers mentioned above are described in Table I. The presence of the ketone or acid in the copolymer and its exact incorporation was determined by means of the infrared spectrum and nitrogen analysis in the case of each different copolymer.

None of these monomers could be homopolymerized using standard free radical procedures for bulk, solution, and emulsion polymerization.

Copolymers of these unsaturated ketones with butadiene will be described elsewhere.

EXPERIMENTAL

General procedure for preparation of pyridine analogs of chalcone. An aqueous 10% sodium hydroxide solution and methanol were added to a three-necked round-bottomed flask equipped with a stirrer and thermometer and the mixture was cooled to 0–10° by surrounding the flask with ice. The stirrer was started and the appropriate aldehyde was introduced in one portion. The acetophenone or acetylpyridine then was added in small portions over a period of an hour keeping the temperature at around 10° ± 1°. The mixture was stirred for three to five hours and the resulting solid was isolated by filtration and was washed thoroughly with water. The solid then was dried and recrystallized three times from 40–50% ethanol.

2-Pyridalacetophenone and its Michael-type addition product with acetophenone. 2-Pyridine aldehyde (175 g., 1.65 moles) and 200 g. (1.65 moles) of acetophenone were used with a liter of 20% sodium hydroxide solution and 50 ml. of ethanol. After isolation the solid was recrystallized from 95% ethanol giving 30 g. of a white crystalline solid, m.p. 119–121°, identified as the Michael-type addition product formed from acetophenone and the desired unsaturated ketone. Its molecular weight as determined by the Rast method is 330, average of two determinations. The calculated value for $C_{22}H_{19}NO_2$ is 329. The infrared spectrum determined in chloroform gave bands at 3015, 1693, 1682, 1600, 1482, 1456, 1445, 1365, 1276, 1210, 1185, 1004, 992, 715, 685 and 668.

Anal. Calc'd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25.
Found: C, 80.15; H, 5.91; N, 4.19.

Water then was added to the mother liquor above to give a 50% alcohol solution, and the resulting solid was recrystallized yielding 145 g. (42%) of pure product; m.p. 60–61°. The

TABLE I

COPOLYMERS OF THE PYRIDINE ANALOGS OF CHALCONE AND CINNAMIC ACID WITH ISOPRENE AND VARIOUS VINYL COMPOUNDS

Monomer	Comonomer	Recipe[a] and Temp.	Time, Hrs.	Conversion, %	Solubility,[b] %	Inherent Viscosity	Softening Point, °C.	Anal. N	Monomer[c] % Incorp.	Polymer Appearance	Infrared[e] Carbonyl and Nitrile Frequencies
2-Pyridalacetophenone	Acrylonitrile	M	24	20	100^d	1.75^d	>200	25.36	5	White powder	2250 cm.$^{-1}$, 1680 cm.$^{-1}$
2-Pyridalacetophenone	Isoprene	M	24	100	100	1.15	—	0.67	10	White elastomer	1679 cm.$^{-1}$
2-Pyridalacetophenone	Methyl acrylate	B	3.5	30	100	0.32	—	.91	12	Tough, elastic	1685 cm.$^{-1}$, 1732 cm.$^{-1}$
2-Pyridalacetophenone	Methyl methacrylate	B	3	90	64	1.10	—	.85	<3	Tough, clear	1727 cm.$^{-1}$
2-Pyridalacetophenone	Styrene	B	3	20	100	0.27	152–160	1.27	19	White powder	1675 cm.$^{-1}$
2-Pyridal-*p*-chloroacetophenone	Acrylonitrile	M	24	20	100^d	1.54^d	>200	25.28	6	White powder	2250 cm.$^{-1}$, 1680 cm.$^{-1}$
2-Pyridal-*p*-chloroacetophenone	Isoprene	M	24	100	100	1.04	—	.68	10	White elastomer	1682 cm.$^{-1}$
2-Pyridal-*p*-chloroacetophenone	Methyl acrylate	B	3.5	30	100	0.34	—	.62	16	Tough	1682 cm.$^{-1}$, 1734 cm.$^{-1}$
2-Pyridal-*p*-chloroacetophenone	Methyl methacrylate	B	3	90	80	1.58	—	.67	<3	Tough, clear	1689 cm.$^{-1}$, 1730 cm.$^{-1}$
2-Pyridal-*p*-chloroacetophenone	Styrene	B	3.5	20	100	0.26	140–145	1.15	20	White powder	1679 cm.$^{-1}$
3-Pyridalacetophenone	Acrylonitrile	M	24	20	100^d	1.57	>200	25.71	4	White powder	1678 cm.$^{-1}$, 2250 cm.$^{-1}$
3-Pyridalacetophenone	Isoprene	M	24	100	40	0.20	—	.75	10	White elastomer	1678 cm.$^{-1}$
3-Pyridalacetophenone	Methyl acrylate	B	3.5	30	100	0.48	—	.50	11	Tough, sticky	1685 cm.$^{-1}$, 1735 cm.$^{-1}$
3-Pyridalacetophenone	Methyl methacrylate	B	3	90	97	1.20	—	.38	<3	Tough, clear	1690 cm.$^{-1}$, 1727 cm.$^{-1}$
3-Pyridalacetophenone	Styrene	B	3.5	20	100	0.24	127–132	1.04	16	White powder	1678 cm.$^{-1}$
4-Pyridalacetophenone	Acrylonitrile	M	24	20	100^d	0.96^d	>200	24.83	7	Pink powder	1680 cm.$^{-1}$, 2250 cm.$^{-1}$
4-Pyridalacetophenone	Isoprene	M	24	100	40	0.20	—	.85	10	White elastomer	1677 cm.$^{-1}$
4-Pyridalacetophenone	Methyl acrylate	B	3.5	30	100	0.47	—	.60	13	Sticky	1682 cm.$^{-1}$, 1735 cm.$^{-1}$
4-Pyridalacetophenone	Methyl methacrylate	B	3	90	70	1.11	—	.35	<3	Tough	1690 cm.$^{-1}$, 1725 cm.$^{-1}$
4-Pyridalacetophenone	Styrene	B	3.5	20	100	0.28	145–150	1.18	18	White powder	1679 cm.$^{-1}$
2-Cinnamoylpyridine	Acrylonitrile	B	8	20	100^d	0.25^d	>200	24.03	11	Purple powder	1695 cm.$^{-1}$, 2250 cm.$^{-1}$
2-Methyl-5-cinnamoylpyridine	Acrylonitrile	M	24	20	100^d	1.90^d	>200	22.79	15	White powder	1681 cm.$^{-1}$, 2250 cm.$^{-1}$
2-Methyl-5-cinnamoylpyridine	Isoprene	M	24	100	100	1.21	—	.60	10	White elastomer	1680 cm.$^{-1}$
2-Methyl-5-cinnamoylpyridine	Methyl acrylate	B	3.5	30	100	0.64	—	.37	8	Sticky	1684 cm.$^{-1}$, 1735 cm.$^{-1}$
2-Methyl-5-cinnamoylpyridine	Methyl methacrylate	B	3	95	86	0.97	—	.20	<3	Tough	1685 cm.$^{-1}$, 1727 cm.$^{-1}$
2-Methyl-5-cinnamoylpyridine	Styrene	B	3.5	20	100	0.26	132–137	.83	14	White powder	1678 cm.$^{-1}$
4-Cinnamoylpyridine	Acrylonitrile	M	24	20	100^d	0.56^d	>200	23.24	15	White powder	2245 cm.$^{-1}$, 1691 cm.$^{-1}$
4-Cinnamoylpyridine	Isoprene	M	24	100	100	1.51	—	0.60	10	White elastomer	1678 cm.$^{-1}$
4-Cinnamoylpyridine	Methyl acrylate	B	3	35	98	0.57	105–110	.62	10	Sticky	1675 cm.$^{-1}$, 1735 cm.$^{-1}$
4-Cinnamoylpyridine	Methyl methacrylate	B	3	90	99	1.33	—	Trace	<3	Tough	1675 cm.$^{-1}$, 1730 cm.$^{-1}$
4-Cinnamoylpyridine	Styrene	B	3	45	100	0.28	—	1.10	16	White powder	1670 cm.$^{-1}$
2-Pyridal-2′-acetylpyridine	Acrylonitrile	B	8	10	100^d	0.16^d	>200	25.37	5	White powder	1693 cm.$^{-1}$, 2245 cm.$^{-1}$
β-(2-Pyridyl)acrylic Acid	Acrylonitrile	A	36	10	100^d	0.34^d	>200	23.38	16	White powder	1720 cm.$^{-1}$, 2245 cm.$^{-1}$
β-(3-Pyridyl)acrylic Acid	Acrylonitrile	A	36	36	100^d	1.08^d	>200	22.26	21	White powder	1718 cm.$^{-1}$, 2245 cm.$^{-1}$
β-(4-Pyridyl)acrylic Acid	Acrylonitrile	A	36	28	100^d	1.35^d	>200	26.70	15	Green powder	1718 cm.$^{-1}$, 2245 cm.$^{-1}$

[a] M = Mutual recipe at 50°, B = Bulk polymerization at 60°, A = Acid side recipe at 50°. [b] Determined in benzene. [c] Based on nitrogen analysis. [d] Determined in dimethyl formamide. [e] Spectra of acrylonitrile copolymers determined in Nujol mull; Isoprene,methyl acrylate, styrene copolymers determined in benzene deposit film; Methyl methacrylate copolymers determined in acetone deposit film.

infrared spectrum of a Nujol mull gave bands at 1669, 1620, 1585, 1454, 1438, 1339, 1223, 1019, 977, 760, and 691. The ultraviolet spectrum gave $\lambda' = 303$ mμ, e $\times 10^{-4} = 2.10$.

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69.

Found: C, 80.36; H, 5.35; N, 6.51.

The *picrate* was prepared as a derivative; m.p. 190–192°.

Anal. Calc'd for $C_{20}H_{14}N_4O_8$: N, 12.79. Found: N, 12.77.

Aldol of 2-pyridalacetophenone. 2-Pyridine aldehyde (10 g., 0.94 mole) and 10 g. of acetophenone (0.85 mole) were used with 100 ml. of sodium hydroxide solution and no methanol. There was isolated 5 g. of a white solid, m.p. 83–84°, which was identified as the aldol. The infrared spectrum of a Nujol mull gave bands at 3140, 1680, 1600, 1445, 1355, 1213, 1107, 1078, 1007, 758, and 687.

Anal. Calc'd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16.

Found: C, 74.16; H, 5.80; N, 6.11.

2-Pyridal-p-aminoacetophenone. *p*-Aminoacetophenone (22 g., 0.16 mole) and 22 g. of 2-pyridine aldehyde (0.20 mole) were used with 400 ml. of sodium hydroxide solution and 200 ml. of methanol. Thus 15 g. (42%) of a bright yellow solid was obtained; m.p. 158–160°. The infrated spectrum of a Nujol mull gave bands at 3410, 3195, 1655, 1620, 1597, 1463, 1452, 1343, 1180, and 783. The ultraviolet spectrum gave $\lambda' = 300$ mμ, e $\times 10^{-4} = 1.45$; $\lambda'' = 375$ mμ, e $\times 10^{-4} = 1.51$; $\lambda''' = 270$ mμ, e $\times 10^{-4} = 1.32$.

Anal. Calc'd for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.49.

Found: C, 74.93; H, 5.44; N, 12.71.

The *picrate* was prepared as a derivative; m.p. 170–171°.

Anal. Calc'd for $C_{20}H_{15}N_5O_8$: N, 15.46. Found: N, 15.75.

2-Pyridal-p-chloroacetophenone. *p*-Chloroacetophenone (154 g., 1 mole) and 200 g. of 2-pyridine aldehyde were used with 400 ml. of sodium hydroxide solution and 200 ml. of methanol. A 50-g. portion of the crude material (140 g.) was purified; m.p. 85–86°. The infrared spectrum of a Nujol mull gave bands at 1670, 1613, 1597, 1473, 1341, 1230, 1094, 1016, 987, 845, and 774. The ultraviolet spectrum gave $\lambda' = 307$ mμ, e $\times 10^{-4} = 1.92$.

Anal. Calc'd for $C_{14}H_{10}ClNO$: C, 69.0; H, 4.14; N, 5.77; Cl, 14.58.

Found: C, 68.77; H, 4.17; N, 5.78.

3-Pyridalacetophenone. Methanol (200 ml.) and 400 ml. of sodium hydroxide solution were used with 214 g. (2 moles) of 3-pyridine aldehyde and 120 g. (1 mole) of acetophenone. After two recrystallizations 127 g. (40%) of a yellow solid was obtained, m.p. 101–102°. The infrared spectrum of a Nujol mull gave bands at 1667, 1613, 1590, 1575, 1458, 1318, 1229, 1020, 987, 769, and 682. The ultraviolet spectrum gave $\lambda' = 298$ mμ, e $\times 10^{-4} = 2.47$.

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69.

Found: C, 80.29; H, 5.28; N, 6.60.

The *picrate* was prepared as a derivative; m.p. 180–181°.

Anal. Calc'd for $C_{20}H_{14}N_4O_8$: N, 12.79. Found: N, 13.05.

4-Pyridalacetophenone and its Michael-type addition product with acetophenone. The reaction was carried out as described above with 214 g. (2 moles) of 4-pyridine aldehyde, 120 g. (1 mole) of acetophenone, and 400 ml. of 10 per cent sodium hydroxide solution. Treatment of the crude product with about 200 ml. of hot alcohol dissolved most of it. The hot solution was filtered and evaporated. The solid obtained from the filtrate was distilled at diminished pressure and then was recrystallized twice from 40% ethanol; 45 g. of a light brown, crystalline solid was obtained; m.p. 70–71°.

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.70.

Found: C, 80.34; H, 5.16; N, 6.88.

The infrared spectrum of a crystalline melt of the compound gave bands at 1670, 1619, 1600, 1553, 1420, 1345, 1304, 1225, 1018, 774, and 691 cm.$^{-1}$. This is consistent with α,β-unsaturated ketone structure.

The *picrate* was prepared as a derivative; m.p. 209–210°.

Anal. Calc'd for $C_{20}H_{14}N_4O_8$: N, 12.79. Found: N, 12.48.

The solid which was separated from the hot alcohol solution of the crude product was recrystallized yielding about 10 g. of white crystalline solid, m.p. 125–126°.

Anal. Calc'd for $C_{22}H_{19}NO_2$: C, 80.25; H, 5.82; N, 4.26.
Found: C, 80.05; H, 5.72; N, 4.42.

The infrared spectrum of a Nujol mull gave bands at 1677, 1603, 1454, 1424, 1220, 1004, 762, 753, and 690 cm.$^{-1}$. This is consistent with the structure of the Michael addition product of 4-pyridalacetophenone and acetophenone.

4-Cinnamoylpyridine. Benzaldehyde (30 g., 0.28 mole) and 30 g. (0.28 mole) of 4-acetylpyridine were used with 200 ml. of sodium hydroxide solution and no methanol. Thus 15 g. (26%) of a yellow crystalline solid was obtained; m.p. 87–88°. The infrared spectrum of a Nujol mull gave bands at 1668, 1607, 1455, 1346, 1232, 1045, 990, 828, 698, and 665. The ultraviolet spectrum gave $\lambda' = 282$ mμ, e $\times 10^{-4} = 1.60$.

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69.
Found: C, 80.59; H, 5.18; N, 6.70.

The *picrate* was prepared as a derivative; m.p. 198–199°.

Anal. Calc'd for $C_{20}H_{14}N_4O_8$: N, 12.79. Found: N, 12.91.

2-Methyl-5-cinnamoylpyridine. Benzaldehyde (40 g., 0.41 mole) and 55 g. (0.41 mole) of 2-methyl-5-acetylpyridine were used with 165 ml. of sodium hydroxide solution and 50 ml. of methanol. Thus 45 g. (49%) of a light yellow solid was obtained; m.p. 74–75°. The infrared spectrum of a Nujol mull gave bands at 1663, 1606, 1457, 1338, 1223, 985, 837, 763, and 698. The ultraviolet spectrum gave $\lambda' = 315$ mμ, e $\times 10^{-4} = 2.24$.

Anal. Calc'd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27.
Found: C, 80.59; H, 5.77; N, 6.27.

The *picrate* was prepared as a derivative; m.p. 228–229°.

Anal. Calc'd for $C_{21}H_{16}N_4O_8$: N, 12.38. Found: N, 12.39.

2-Cinnamoylpyridine. The synthesis of 2-cinnamoylpyridine (6) has been improved. The same procedure was employed as that reported above for 4-cinnamoylpyridine with 2-acetylpyridine substituted for the 4-acetylpyridine. There was obtained 35 g. (61%) of a light green solid, m.p. 71–72°. The infrared spectrum of a Nujol mull gave bands at 1668, 1607, 1575, 1553, 1338, 1221, 1022, 987, and 750. The ultraviolet spectrum gave $\lambda' = 318$ mμ, e $\times 10^{-4} = 1.86$.

The *picrate* was prepared as a derivative; m.p. 121–122°.

Anal. Calc'd for $C_{20}H_{14}N_4O_8$: N, 12.79. Found: N, 12.63.

2-Pyridal-2'-acetylpyridine. 2-Pyridine aldehyde (14 g., 0.13 mole) and 9 g. (0.075 mole) of 2-acetylpyridine were used with 35 ml. of sodium hydroxide solution and no methanol. Thus 7 g. (40%) of a yellow crystalline solid was obtained; m.p. 62–64°. The infrared spectrum of a crystalline melt gave bands at 1674, 1615, 1587, 1571, 1442, 1334, 1025, 993, and 738. The ultraviolet spectrum gave $\lambda' = 304$ mμ, e $\times 10^{-4} = 1.30$.

Anal. Calc'd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.80; N, 13.33.
Found: C, 74.16; H, 4.63; N, 13.12.

The *picrate* was prepared as a derivative; m.p. 142°.

Anal. Calc'd for $C_{19}H_{13}N_5O_8$: N, 15.95. Found: N, 15.86.

Aldol of propiophenone and 2-pyridine aldehyde. The procedure for the preparation of 2-pyridalacetophenone was followed and the sole product isolated was a white crystalline solid in 40% yield identified as the aldol; m.p. 95–96°. The infrared spectrum of a Nujol mull gave bands at 3140, 1684, 1604, 1457, 1227, 1123, 999, 966, 742, and 690.

Anal. Calc'd for $C_{15}H_{15}NO_2$: C, 74.70; H, 6.28; N, 5.87.
Found: C, 74.65; H, 5.99; N, 5.97.

Distillation of the solid under diminished pressure gave propiophenone as the only identifiable product. Attempts to dehydrate the aldol by refluxing with acid and/or iodine were unsuccessful.

4-Acetylpyridine. The method of Kolloff and Hunter (13) starting with ethyl isonicotinate was used. Yield, 90 g., b.p. 64.5–65.5°/2.1 mm.

PREPARATION OF PYRIDINE ANALOGS OF CINNAMIC ACID

β-(3-Pyridyl)acrylic acid. This acid was prepared by a modification of the method of Pannizon (7). 3-Pyridine aldehyde (32 g., 0.3 mole) and 31.4 g. (0.3 mole) of malonic acid were placed in a 300-ml. round-bottomed flask along with 23.7 g. of pyridine and 6 drops of piperidine. After heating for two hours on a steam-bath, the solid formed was washed with water and dried. A white solid was obtained on purification (9) (20 g., 45%); m.p. 233° with decomp. The infrared spectrum of a Nujol mull gave bands at 2440, 1700, 1586, 1423, 1314, 1286, 987, 811, and 687. The ultraviolet spectrum gave $\lambda' = 257$ mμ, e × $10^{-4} = 1.18$.

Anal. Calc'd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39.
Found: C, 69.26; H, 4.51; N, 9.31.

β-(2-Pyridyl)acrylic acid. 2-Pyridine aldehyde was substituted in the procedure above and 20 g. (45%) of a white solid, m.p. 198° with decomp., was obtained. The infrared spectrum of a Nujol mull gave bands at 2400, 1700, 1647, 1599, 1450, 1320, 1227, 1202, 1014, 984, 788, and 745. The ultraviolet spectrum gave $\lambda' = 288$ mμ, e × $10^{-4} = 1.12$; $\lambda'' = 2.48$ mμ, e × $10^{-4} = 1.16$.

Anal. Calc'd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39.
Found: C, 64.42; H, 4.56; N, 9.36.

β-(4-Pyridyl)acrylic acid. 4-Pyridine aldehyde was substituted in the procedure for the preparation of the three isomers above and 22 g. (49%) of a white solid was obtained; m.p. 295° with decomp. The infrared spectrum of a Nujol mull gave bands at 2400, 1700, 1612, 1420, 1317, 1225, 1187, 1022, 994, 965, and 825. The ultraviolet spectrum gave $\lambda' = 257$ mμ, e × $10^{-4} = 1.52$.

Anal. Calc'd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39.
Found: C, 64.14; H, 4.59; N, 9.62.

POLYMERIZATION RECIPES AND TECHNIQUES

GR-S Mutual recipe. The recipe of Frank and co-workers (10), adapted to a monomer charge of 5 g., was used in this study. Potassium persulfate (1 ml. of 3% aqueous solution) was used as initiator and 0.0176 g. of Hooker's lauryl mercaptan (a mixture of primary mercaptans having the average molecular formula $C_{12.6}H_{26.2}SH$) was used as modifier.

Acid side recipe. The recipe of Potts (11) was modified as shown below.

Water (boiled and cooled under nitrogen to eliminate oxygen)	20 ml.
MP-635-S[1]	2 ml.
Azobisisobutyronitrile	0.03 g.
Monomers	5.0 g.
Hooker's lauryl mercaptan	0.0176 g.

Bulk recipe. A five-gram monomer charge was used with 0.04 g. of azobisisobutyronitrile as initiator at 60°.

Solution recipe. The bulk recipe was used with 10 ml. of benzene or dimethylformamide as solvent.

Polymerizations. Polymerizations were carried out in 4-ounce screw cap bottles sealed with self-sealing rubber gaskets. Bottles were charged in the order listed in the recipes and then tumbled in a constant temperature bath. The bottles were not tumbled in the bulk polymerizations at 60°.

Inherent viscosities (12). These were determined in Ostwald viscometers in either benzene or dimethylformamide solution at 25°.

Table I describes the copolymers and the conditions for their preparation.

UNSUCCESSFUL POLYMERIZATION REACTIONS

Isobutyl vinyl ether. No polymeric product was isolated after 72 hours using the bulk recipe with any of these pyridyl ketones.

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[1] We are indebted to Dr. Stanley Detrick of E. I. duPont deNemours and Company for the emulsifier. Its composition is as follows:

Sodium alkanesulfonates in the C_{16} range	49.5%
Unreacted hydrocarbon	10.3%
Sodium chloride	0.86%
Sodium sulfate	0.4%

Balance, water and about 3% isopropyl alcohol.

Maleic anhydride. No polymer was isolated after 36 hours using the bulk recipe with any of these ketones.

2-Vinylpyridine. No polymer could be isolated after a day using the bulk recipe with any of the ketones although the 2-methyl-5-cinnamoylpyridine and 3-pyridalacetophenone mixtures thickened.

Vinyl acetate and vinyl chloride. No polymers could be isolated with these monomers after a day in the Mutual recipe or twelve hours in the bulk recipe with any of the ketones. No polymer could be isolated with vinyl acetate in the acid side recipe with any of the pyridylacrylic acids.

Styrene, methyl acrylate, and methyl methacrylate. Products were formed with these monomers and the β-pyridylacrylic acids but the acid was not incorporated in the polymer. No polymers could be isolated with these monomers and 2-cinnamoylpyridine or 2-pyridal-2′-acetylpyridine using the bulk recipe after 12 hours.

Isoprene. 2-Cinnamoylpyridine and 2-pyridal-2′-acetylpyridine did not form copolymers with isoprene after 24 hours using solution polymerization with 10 ml. of benzene as solvent.

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SUMMARY

A series of pyridine analogs of chalcone and cinnamic acid have been prepared and their preparation has been described in detail along with the infrared and ultraviolet absorption spectra.

Some polymerizations and copolymerizations of these new monomers have been described and the properties of a variety of new copolymers have been recorded.

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