a single nmr absorption, at 6.66 ppm, but was differentiated from **9** by its infrared spectrum and glc retention time. The structure of **3** then corresponds, by elimination of possibilities, to α,β,2,3,4,5,6-heptachlorostyrene.

Experimental Section

General.—Melting points were taken in glass capillaries and are uncorrected. The ir spectra were determined in carbon tetrachloride solution using a Beckman IR-4 spectrophotometer. The nmr spectra were determined in deuteriochloroform using a Varian A-60 spectrophotometer, with TMS as the internal standard. Gas chromatography was carried out using a Varian Aerograph A-90P instrument equipped with a thermal conductivity detector, on a 5 ft × 0.25 in. stainless steel column containing 20% SE-30 on Chromosorb W, at 230°. Perchlorinated styrene and vinylpyridine starting materials were prepared according to a published vapor phase chlorination procedure.[12]

An undivided cell containing as electrodes either alternating plates of sheet lead and graphite or a pool of mercury stirred by a magnetic bar and faced by a graphite disk was used with a calomel reference electrode and an NJE Model RVC-36-25 M potentiostat. In all experiments, oxidation of methanol was the principal anode reaction. Reactant concentrations were 0.1–0.15 mol/l., and electrolyte concentrations were 0.1, 0.5, and 1.0 *M* for hydrochloric acid, ammonium chloride, and ammonium acetate, respectively. Cathode current densities were 0.005–0.02 A/cm² and current efficiencies ranged from 50 to 80% based on a transfer of four electrons per molecule. The cathode potentials were maintained at values corresponding to the least amount of overreduction for a given reaction, as determined by following the course of reaction by glc, and were within the range −0.7 to −1.5 V (*vs.* sce). The cathode was generally partly covered at the end of the reaction by a yellow amorphous film which was not identified.

Reduction of Octachlorostyrene (1).—The following example, corresponding to run 2 of Table I, is illustrative. A mixture of 70.0 g (0.185 mol) of octachlorostyrene, 1 l. of methanol, 1.2 l. of dimethoxyethane, 20 ml of concentrated aqueous ammonia, 150 g of ammonium acetate, and 100 ml of water was warmed to 60° until complete solution was effected and then placed in a cell equipped with alternating plates, three each, of sheet lead (0.2-cm thickness) and graphite (0.5-cm thickness). The gross working lead cathode surface was 470 cm². Electrolysis was carried out with vigorous stirring at a cathode potential of −1.2 V (*vs.* sce) resulting in an average flow of 10-A current, or an average current density of 0.021 A/cm². After 2 hr, glc analysis indicated a conversion of 86% and product distribution as shown in Table I. The reaction solution was drained from the cell and 250 ml of water was added. Overnight cooling resulted in the separation of 26.4 g of pentachloroethynylbenzene (**2**): ir 3280 (≡CH) and 2200 cm⁻¹ (C≡C), mp 180–182° (lit.[6] mp 185–186°). The mother liquor was further diluted with water (3 l.) and extracted with dichloromethane (three 500-ml) portions. Preparative glc of the concentrated extract resulted in the isolation of β,β-2,3,4,5,6-heptachlorostyrene (**3**) and 2,3,-5,6-tetrachloroethynylbenzene (**4**). The properties of these and subsequent products are given in Table II (p 2001).

From a reaction similar to the above, but electrolyzed 4 hr at −1.4 V (*vs.* sce) to favor overreduction, preparative glc of the crude product resulted in the isolation of 2,3,5,6-tetrachlorostyrene (**5**), the major product.

Reduction of Heptachloro-2-vinylpyridine (6a) and Heptachloro-3-vinylpyridine (6b).—Reduction was carried out in essentially the same fashion as described above. The crude product from **6a** contained 50.6% tetrachloro-2-ethynylpyridine (**7a**), isolated in pure form by crystallization from ethanol, 13.0% *trans*-β,3,4,5,6-pentachloro-2-vinylpyridine (**8**), isolated in pure form by preparative glc, 17.6% a third product which was not identified, and 18.8% unreacted **6a**.

The crude product from **6b** contained 50.7% tetrachloro-3-ethynylpyridine (**7b**), isolated in pure form by crystallization from ethanol, 22.4% two other products which were not identified, and 26.9% unreacted **6b**.

Addition of Chlorine to Pentachloroethynylbenzene (2).—Chlorine gas was bubbled through a stirred solution of 10 g (0.04 mol) of **2** in 150 ml of carbon tetrachloride at the rate of *ca.* 10 ml/min. After 30 hr, most of the **2** disappeared and two major products were formed in the ratio of 2.5:1. Evaporation of the solvent gave 14.4 g of an oil which partially solidified on standing. Two recrystallizations from acetone gave 1.5 g of the major component (**9**) as tan crystals. From the concentrated mother liquors, the minor component (**10**) was obtained as a colorless oil by preparative glc.

(12) W. H. Taplin (Dow Chemical Co.), U. S. Patent 3,420,833 (1969).

Registry No.—**1**, 29082-74-4; **3**, 29082-75-5; **4**, 29082-76-6; **5**, 29082-77-7; **6a**, 22652-20-6; **6b**, 29086-34-8; **7a**, 29086-35-9; **7b**, 29086-36-0; **8**, 29086-37-1; **9**, 29086-38-2; **10**, 29086-39-3.

The Hammick Reaction of Methoxypyridine-2-carboxylic Acids with Benzaldehyde. Preparation of Methoxy-2-pyridyl Phenyl Ketones

ELLIS V. BROWN* AND M. B. SHAMBHU

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

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The Hammick reaction,[1,2] synthesis of carbinols by thermal decarboxylation of certain heterocyclic carboxylic acids in the presence of carbonyl compounds, has been widely used in the preparation of a number of 2-pyridyl carbinols.[3,4] Thus far the only substituted pyridine-2-carboxylic acids used as substrates in the Hammick reaction have been the methylpyridine acids.[4] The corresponding carbinols have been obtained by thermal decomposition of these acids in benzaldehyde and anisaldehyde in yields ranging from 35 to 53%. In the present study, synthesis of the methoxypyridine-2-carboxylic acids and their thermal decomposition in benzaldehyde are described. In each case two products, the corresponding methoxy-2-pyridyl phenyl carbinol and the methoxypyridine, were obtained. The carbinols were oxidized to the corresponding ketones by chromic acid solution.

Reaction Medium.—In each case, 1 g of the acid was heated with 6 g of benzaldehyde and 6 g of *p*-cymene. The use of *p*-cymene has been found to increase the yield of the Hammick product.[3,4] All the methoxy acids are soluble in this reaction medium above 90° and insoluble at 25°. The highest temperature for the reaction was 175°, the reflux temperature.

General Procedure.—The finely divided acid was added in one portion to the reaction medium. The mixture was stirred under nitrogen and heated below the decarboxylation temperature until a clear solution was obtained. It was then brought up to the reaction temperature and maintained there for the desired period. On cooling overnight, the unreacted acid, if any, was removed by filtration. The solution was then extracted three times with hydrochloric acid (15%) and the acid extracts were washed with petroleum ether.

(1) (a) D. L. Hammick and P. Dyson, *J. Chem. Soc.*, 1724 (1937); (b) D. L. Hammick and P. Dyson, *ibid.*, 809 (1939).

(2) (a) D. L. Hammick and B. R. Brown, *ibid.*, 173 (1949); (b) D. L. Hammick and B. R. Brown, *ibid.*, 659 (1949).

(3) N. Sperber, D. Papa, E. Schwenk, and M. Sherlock, *J. Amer. Chem. Soc.*, **71**, 887 (1949).

(4) N. H. Cantwell and E. V. Brown, *ibid.*, **75**, 1489 (1953).

TABLE I

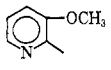
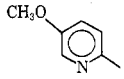
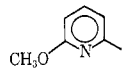
HAMMICK REACTION OF METHOXYPYRIDINE-2-CARBOXYLIC ACIDS IN BENZALDEHYDE AND *p*-CYMENE[a]

Pyridine-2-carboxylic acid	ΔG^*,[b] kcal	Temp, °C	Time, hr	Acid used g	Acid used mmol	Carbinol obtained g	Carbinol obtained mmol	Methoxypyridine obtained g	Methoxypyridine obtained mmol	%[c] carbinol	%[c] methoxypyridine	Ratio of C/M
6-Methoxy-	37.8	174–175	36[d]	10.0	65.4	1.5	7.0	0.6	5.5	10.7	8.4	1.3
6-Methoxy-	37.8	174–175	72[d]	10.0	65.4	2.6	12.2	1.0	9.2	18.6	14.1	1.3
5-Methoxy-	35.9	174–175	12[d]	6.0	39.2	3.8	17.7	1.4	12.8	45.2	32.7	1.4
5-Methoxy-	35.9	174–175	18	6.0	39.2	4.7	21.8	1.7	15.7	55.5	40.2	1.4
4-Methoxy-	32.2	168–170	3	6.0	39.2	4.9	22.7	1.6	14.7	58.0	37.5	1.6
3-Methoxy-	29.0	100–103	2	2.1	13.8	2.0	9.3	0.4	3.7	67.5	27.0	2.5

[a] In 1:6:6 ratio. [b] Reproduced from ref 6. [c] No correction for unreacted acid. [d] Unreacted acid recovered.

TABLE II

PHYSICAL AND SPECTRAL PROPERTIES OF CARBINOLS, $RCHOHC_6H_5$

R =	Registry no.	Mp or bp, °C	Ir[a] (OH), cm^{-1}	Nmr,[b] δ, ppm ($CDCl_3$ solvent)	Mass spectra, *m/e* (rel intensity)
	29082-98-2	116.5	3600 (v broad, large)	3.7 (s, 3, OCH_3), 5.5 (br, 1, OH); 5.9 (s, 1, CHOH), 7.15 (m, 2, py), 7.35 (s, 5, C_6H_5), 8.2 (m, 1, py)	215 (100), 200 (23), 154 (11), 138 (70), 110 (30), 109 (34), 108 (68), 94 (15), 80 (10)
	29082-99-3	42	3600, 3400	3.7 (s, 3, OCH_3), 5.4 (br, 1, OH), 5.75 (s, 1, CHOH), 6.6–6.9 (m, 2, py), 7.3 (s, 5, C_6H_5), 8.3 (m, 1, py)	215 (100), 214 (47), 198 (11), 138 (45), 109 (44), 108 (17)
	29086-45-1	77	3600, 3400	3.75 (s, 3, OCH_3), 5.0 (br, 1, OH), 5.65 (s, 1, CHOH), 6.9–7.1 (m, 2, py), 7.3 (s, 5, C_6H_5), 8.1 (m, 1, py)	215 (100), 198 (46), 154 (53) 138 (10), 94 (20), 85 (60), 69 (70), 43 (46)
	29083-00-9	160–162 (2 mm)	3600, 3400	3.95 (s, 3, OCH_3), 4.8 (br, 1, OH), 5.7 (s, 1, CHOH), 6.7 (m, 1, py), 7.2–7.7 (m, 8, C_6H_5 and py)	215 (100), 138 (16), 131 (26), 110 (41), 109 (84), 108 (30), 105 (40), 94 (20), 93 (27), 80 (15)

[a] In $CHCl_3$, 2–6% solution. [b] py = pyridine protons; br = broad peak.

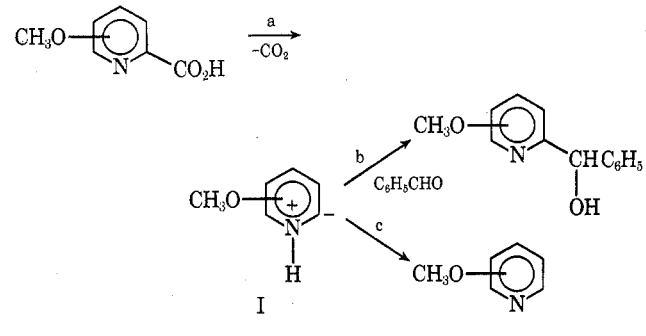
After addition of sodium hydroxide solution (to pH 9), the basic products (methoxypyridine and carbinol) were extracted with ether. After removal of ether, the two products were separated by distillation, the methoxypyridine having a much lower boiling point. In the case of solid carbinols, these were also separated by filtration; the methoxypyridines were removed by washing with water and isolated from the filtrate by ether extraction. The carbinols were converted to the ketones by chromic acid oxidation as described earlier.[5]

Results and Discussion

The results of a few runs are reported in Table I. Over 90% of the acids have been accounted for by the two products except in the case of the 6-methoxy acid. This acid reacts very slowly at 175°, the reaction not being complete even after 72 hr.

The kinetics of decarboxylation of these methoxy acids in *m*-nitrotoluene have been studied by Moser[6] and the free energies of activation, ΔG^* (Table I), were calculated from the rate constants at various temperatures. Decarboxylation was found to be most facile in the case of the 3-methoxy acid (lowest ΔG^*, rate constant at 100.9° = 3.14×10^{-4} sec^{-1})[6] and most difficult in the case of the 6 isomer (highest ΔG^*, rate constant at 200.0° = 0.33×10^{-4} sec^{-1}).[6] As seen in Table I, the 3-methoxy acid gives the highest yield of the carbinol and the 6 isomer the lowest yield.

The formation of the two products may be shown as follows. The slow or rate-determining step a results in the formation of the reactive intermediate I which then



I

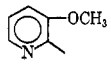
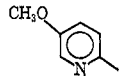
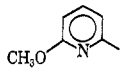
reacts in the subsequent fast or product-determining steps b and c. The product ratio, carbinol to methoxypyridine, reflects the relative rates of steps b and c. This ratio is seen to be increasing with the ease of decarboxylation (lower ΔG^*), being the highest for the 3-methoxy acid. The intermediate I formed at lower temperature is expected to be less energetic (more stable). As the stability of I increases, step b is seen to become faster than step c, resulting in a higher yield of the carbinol.

Step c involves only a proton transfer (known as a fast process), while step b involves reaction of I with benzaldehyde. For step b to be faster than step c, the benzaldehyde molecules (which are in excess) must occupy favorable positions around intermediate I. This may also be visualized as a concerted process.[7]

(5) E. V. Brown and M. B. Shambhu, *Org. Prep. Proced.*, **2**, 285 (1970).
(6) R. Moser, Ph.D. Thesis, University of Kentucky, 1970.
(7) K. Schofield, "Hetero-aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967, pp 163 and 319.

TABLE III

PHYSICAL AND SPECTRAL PROPERTIES OF KETONES, $RCOC_6H_5$

R =	Registry no.	Mp or bp, °C	Ir[a] (C=O), cm^{-1}	Nmr,[b] δ, ppm ($CDCl_3$ solvent)	Calcd for $C_{13}H_{11}NO_2$: C, 73.24; H, 5.17; N, 6.57
	19974-93-7	34–35, 174–175 (3 mm)	1660	3.8 (s, 3, OCH_3), 7.2–7.5 (m, 5, Ar), 7.6–7.8 (m, 2, Ar), 8.1 (m, 1, py)	C, 73.03; H, 4.97; N, 6.47
	29082-95-9	45–46	1640	3.9 (s, 3, OCH_3), 7.0 (m, 1, py), 7.3–7.6 (m, 4, Ar), 8.0–8.2 (m, 2, Ar), 8.5 (m, 1, py)	C, 73.62; H, 5.01; N, 6.42
	29082-96-0	75	1650	3.9 (s, 3, OCH_3), 7.2–7.6 (m, 4, Ar), 8.0–8.2 (m, 3, Ar), 8.4 (m, 1, py)	C, 72.94 H, 5.27; N, 6.22
	29082-97-1	124–127 (2 mm), 40–42	1640	3.9 (s, 3, OCH_3), 6.9 (m, 1, py), 7.3–7.8 (m, 8, Ar)	C, 73.04; H, 4.98; N, 6.32

[a] In $CHCl_3$, 2–6% solution. [b] Py = pyridine protons.

Experimental Section

All melting points are uncorrected and were obtained using the Fisher-Johns melting block. Infrared spectra were recorded with a Beckman IR-8 spectrometer. Nmr spectra were taken on a Varian Model A-60 spectrometer; chemical shifts are reported in parts per million (δ) from TMS as the internal standard. The mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E spectrometer at 70 eV and 200°. The properties of the carbinols and ketones are reported in Tables II and III. The general procedure for the Hammick reaction has already been described.

3-Methoxypyridine-2-carboxylic Acid.—A solution of 6.0 g (0.032 mol) of 2-bromo-3-methoxypyridine[8] in 50 ml of anhydrous ether was added to a solution of *n*-butyllithium (0.06 mol) in 50 ml of ether at −40 to −50° over a period of 30 min. The resulting red mixture was stirred for 15 min below −40° and then poured into a slurry of excess Dry Ice in 200 ml of ether. After standing overnight, the ethereal slurry was extracted with 50 ml of water. The aqueous extract was washed twice with 20 ml of benzene, the benzene extracts being discarded. The aqueous solution was made acidic (pH 4) by the addition of 48% hydrobromic acid solution. A saturated solution of copper sulfate was added. After cooling in an ice bath, the grey precipitate of the copper salt was removed by filtration and washed with two 5-ml portions of cold water. The copper salt was then suspended in 50 ml of water and copper sulfide was precipitated by bubbling hydrogen sulfide through the warm solution. After removal of copper sulfide by filtration, the filtrate was evaporated to dryness at room temperature. The crude acid (2.8 g) was recrystallized from methanol (1.8 g, 37%): mp 130° (rapid decomposition); nmr (DMSO-d_6) δ 3.85 (s, 3, OCH_3), 7.41–7.55 (m, 2, pyridine-4 and -5 protons), 8.18 (m, 1, pyridine-6 proton), and 11.4 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 54.92; H, 4.57; N, 9.15. Found: C, 54.61; H, 4.65; N, 8.96.

4-Methoxypyridine-2-carboxylic Acid.—To a solution of 3.2 g (0.14 g-atom) of sodium in 150 ml of methanol, 4-nitropyridine-2-carboxylic acid[8] (5.0 g, 0.030 mol) was added. The mixture was refluxed for 2 hr and the methanol was removed by distillation. The residue was treated with hydrochloric acid until pH 3 was attained. The methoxy acid (3.9 g, 85%) was obtained *via* the copper salt as colorless crystals: mp 204° dec; nmr (DMSO-d_6) δ 3.95 (s, 3, OCH_3), 7.3 (m, 2, pyridine protons), 8.1 (m, 1, pyridine proton), and 11.2 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 54.92; H, 4.57; N, 9.15. Found: C, 54.61; H, 4.51; N, 9.06.

5-Methoxypyridine-2-carboxylic Acid.—To a solution of 12.3 g (0.1 mol) of 5-methoxy-2-methylpyridine[9] in 350 ml of water, 70 g (0.44 mol) of potassium permanganate was added in ten portions over 3 hr. The mixture was vigorously stirred and maintained at 90–95°. The hot mixture was filtered and the filtrate was made acidic (pH 4) by addition of hydrochloric acid after cooling. The acid (7.2 g, 47%) was isolated *via* the copper salt: mp 167°; nmr ($CDCl_3$) δ 3.85 (s, 3, OCH_3), 7.4–7.9 (m, 2, pyridine protons), 8.3 (m, 1, pyridine protons), and 9.8 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 54.92; H, 4.57; N, 9.15. Found: C, 54.62; H, 4.49; N, 9.08.

6-Methoxypyridine-2-carboxylic Acid.—To a solution of 6 g (0.26 g-atom) of sodium in 150 ml of methanol, 11 g (0.054 mol) of 6-bromopyridine-2-carboxylic acid[10] (made by the oxidation of 6-bromo-2-methylpyridine[11] using potassium permanganate) was added. The mixture was refluxed for 6 hr and the methanol was removed by distillation. To the residue 100 ml of water was added and the aqueous solution was made acidic (pH 2) by hydrochloric acid. The methoxy acid was removed by filtration (7 g, 84%): mp 129–130°; nmr ($CDCl_3$) δ 4.0 (s, 3, OCH_3), 7.0 (m, 1, pyridine-4 proton), 7.8 (m, 2, pyridine protons), and 9.2 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 5.492; H, 4.57; N, 9.15. Found: C, 54.67; H, 4.44; N, 9.21.

Registry No.—Benzaldehyde, 100-52-7; 3-methoxypyridine-2-carboxylic acid, 16478-52-7; 4-methoxypyridine-2-carboxylic acid, 29082-91-5; 5-methoxypyridine-2-carboxylic acid, 29082-92-6; 6-methoxypyridine-2-carboxylic acid, 26893-73-2.

(8) E. V. Brown, *J. Amer. Chem. Soc.*, **76**, 3167 (1954).
(9) L. Marion and W. F. Cockburn, *ibid.*, **71**, 3403 (1949).
(10) H. Gilman and S. M. Spatz, *J. Org. Chem.*, **16**, 1485 (1951).
(11) H. P. T. Willink, Jr., and J. P. Wilbaut, *Recl. Trav. Chim. Pays-Bas*, **53**, 417 (1934).

Improved Preparation of 6-Methoxybenzoxazolinone[1]

EDWARD H. ALLEN* AND SUSAN K. LAIRD

Plant Science Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Maryland 20705

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6-Methoxybenzoxazolinone (IV) has been implicated as a natural factor for the resistance of corn (*Zea mays L.*) to disease and insect attack.[2,3] To evaluate the role of IV as a disease resistance factor in Helmin-

(1) Mention of a trademark name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the U. S. Department of Agriculture, and does not imply its approval to the exclusion of other products that may also be suitable.
(2) A. Stoessl in "Recent Advances in Phytochemistry," Vol. III, C. Steelink and V. C. Runeckles, Ed., Appleton-Century-Crofts, New York, N. Y., 1970.
(3) S. D. Beck, *Ann. Rev. Entomol.*, **10**, 207 (1965).