PYRROLE CHEMISTRY

IV. THE PREPARATION AND SOME REACTIONS OF BROMINATED PYRROLE DERIVATIVES

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ABSTRACT

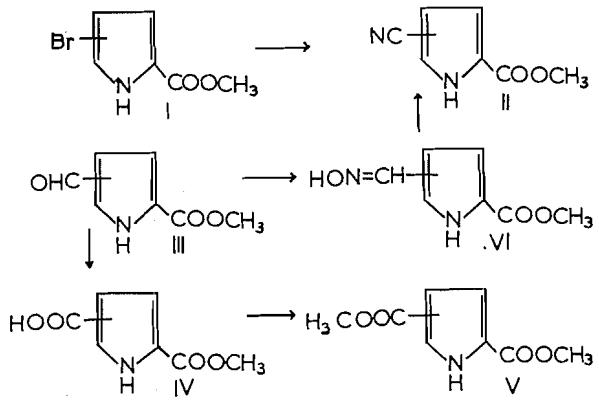
Methyl 2-pyrrolecarboxylate and 2-pyrrolecarboxaldehyde have been brominated under a variety of conditions and the isomer ratios determined. The products have been identified as the 4-bromo, 5-bromo, and 4,5-dibromo derivatives and their structures proved. It has been shown that the bromine group in these products is not easily displaced by nucleophiles although this has been accomplished with the cyanide ion. The bromine has been removed easily by catalytic hydrogenation.

In our survey of the reactions of relatively simple pyrrole derivatives (1) it appeared likely that bromination might prove both useful and interesting. A selection of types of brominating agents including molecular bromine, the bromonium ion, and the bromine atom is available (2). In turn it might prove possible to replace the bromine group by others such as cyanide or methoxyl as has been done in the thiophene and furan series (3, 4, 5). The most satisfactory starting materials appeared to be methyl 2-pyrrolecarboxylate and 2-pyrrolecarboxaldehyde. The electron-withdrawing groups would provide a 4-directing effect. Thus a mixture of 4- and 5-isomers would be formed (1, 6) which might be made to favor one or the other position by a choice of the type of brominating agent. In addition, both ester and aldehyde can be converted to the acid group which then might be removed by decarboxylation. Finally, the deactivation of an electron-withdrawing group would be necessary to allow the isolation of monobrominated products in reasonable yields (7). From the reaction products we isolated 4-bromo, 5-bromo, and 4,5-dibromo derivatives for both the 2-ester and the 2-aldehyde. A small amount of the 3,4,5-tribromo-2-ester (8) was also found in one reaction. Methyl 4,5-dibromo-2-pyrrolecarboxylate (9) has been reported previously.[1]

Identification of the monobrominated-2-esters (I) was accomplished by a series of reactions. First, nucleophilic displacement of the bromine group was carried out using cuprous cyanide in hot dimethyl sulfoxide. The yields of methyl 4- and 5-cyano-2-pyrrolecarboxylate (II) were not good but in each case a single product was obtained and characterized. Then methyl 2-pyrrolecarboxylate was formylated by the Vilsmeier-Haack technique (3) producing a mixture (III), containing mostly the 4-formyl-2-ester along with some of the 5-formyl-2-ester. Pinder (10) has formylated the corresponding ethyl ester but obtained a considerably greater proportion of 5-formylation. Each formyl-2-ester was then subjected to two operations. First, it was oxidized (IV) and esterified (V) to the known methyl 2,5- or 2,4-pyrroledicarboxylate (11), thus proving the orientation of substituents. A second portion of each formyl-2-ester was converted to the oxime (VI), dehydrated to the corresponding 4- or 5-cyano-2-ester and used for mixed melting point and comparison of infrared spectrum with the products (II) obtained above. Further

[1]*Dr. R. W. Rickards of the University of Manchester has kindly informed us that he and P. Hodge have brominated the 2-ester with bromine in acetic acid and obtained and identified the same products. The physical properties of the products are in agreement with ours.*

bromination of either monobrominated ester led to the same dibrominated product. The same was true for the monobrominated aldehydes. The monobromo-2-aldehydes were oxidized and esterified to the corresponding monobromo-2-esters (I) for identification. The dibromo-2-aldehyde was treated similarly.



In addition, the nuclear magnetic resonance (n.m.r.) spectra of the brominated esters and aldehydes had already provided quite adequate identification. As has been observed for the benzene series (12), bromination does not greatly alter the positions of the signals of the remaining aromatic protons from those of the parent compounds. These results will be discussed in a forthcoming paper.

After isolation of all the pure substances from the bromination reactions using column chromatography on alumina and fractional crystallization, further trials were analyzed by gas–liquid partition chromatography. A series of trials with known mixtures showed that the triangulation method of analysis could be applied to the gas chromatograms with an accuracy of about 2%. The results were converted to mole % and are recorded in the tables. It was soon found that from a preparative point of view bromination in carbon tetrachloride, with a trace of iodine, was by far the best reaction. No other method approached the greater than 90% conversions possible for the ester. Although the acetic acid reaction was satisfactory the work-up was more laborious.

Several conclusions may be drawn from Table I, which lists a representative selection from a large number of trials on ester and aldehyde. Bromination at the 4-position predominates at room temperature and below, where the 4- : 5- substitution ratio is usually from 6:1 to 10:1. At the boiling point of carbon tetrachloride the attack is much less selective and the amount of 5-bromo product present approaches that of the 4-bromo. The former may then be isolated easily by column chromatography. Increasing the relative amount of bromine raises the percentage of dibrominated product and may produce almost a quantitative yield of it if desired. Conversions are generally lower for the aldehyde brominations than for those of the ester. There is little destruction of the pyrrole nucleus under these conditions.

Of the variety of other reagents listed in Table II none proved to be a selective reagent for attack at the 5-position. The only satisfactory procedures found by us for obtaining 5-bromo derivatives involve the most vigorous reagents and conditions. Under these circumstances the amounts of 4- and 5-bromination are about equal. The free radical reagent N-bromosuccinimide in carbon tetrachloride, with some benzoyl peroxide, was equally random. No 3-bromination was detected in any of our experiments.

TABLE I

Brominations in carbon tetrachloride

t (min)	Temp.	Conversion*	4-Bromo*	5-Bromo*	4,5-Dibromo*
		(*a*) Methyl 2-pyrrolecarboxylate			
90	0°	74.9	68.4	6.5	—
10	28°	69.6	58.4	9.5	1.7
30	28°	84.9	74.1	7.6	3.2
60	28°	96.9	83.1	11.9	1.9
90	28°	97.6	82.8	12.5	2.3
90	70°	84.3	46.5	31.4	6.4
120	28°	100.0†	15.6	2.3	82.1
20	70°	100.0†	49.0	38.1	12.9
90	70°	100.0†	46.3	35.0	18.7
120	28°	100.0‡	2.0	—	98.0
		(*b*) 2-Pyrrolecarboxaldehyde			
90	0°	62.8	60.7	2.1	—
90	28°	74.7	62.3	11.0	1.4
90	70°	66.0	26.0	24.0	16.0
120	28°	100.0§	5.2	0.4	94.4

*Values in mole %, mole ratio 1:1 (except †, ‡, and §).
†Mole ratio ester : bromine = 1:1.25.
‡Mole ratio ester : bromine = 1:2.
§Mole ratio aldehyde : bromine = 1:2.

TABLE II

Bromination of methyl 2-pyrrolecarboxylate*

Reagent†	Conversion	4-Bromo	5-Bromo	4,5-Dibromo
(*a*) Br_2/Fe	69.6	47.5	16.7	5.4
(*b*) $Br_2/AlCl_3$	64.5	29.1	29.7	5.7
(*c*) Br_2/dioxane	68.0	38.0	16.4	13.6
(*d*) Br_2/HOAc	36.3	12.3	3.3	20.7
(*e*) NBS/peroxide	40.7	15.3	14.2	11.2
(*f*) $Br_2/AgClO_4/HClO_4$	35.3	14.9	5.2	15.2
(*g*) $HOBr/H_3O^+$	6.2	4.7	0.4	1.1
(*h*) Pyridinium bromide perbromide	55.7	49.1	1.8	4.8
(*i*) NaOBr/NaOH	22.2	20.5	1.7	—
(*j*) CuBr/DMF	6.3	3.3	3.0	—

*Values in mole %, mole ratio ester : reagent = 1:1 throughout.
†See Experimental for description of reagent, time, and temperature.

The bromonium ion from acidified hypobromous acid (13) or from bromine and silver perchlorate in perchloric acid (prepared analogously to the chloronium ion of ref. 14), was neither very selective nor very successful. Basic reagents such as bromine in dilute aqueous sodium hydroxide and pyridinium bromide perbromide in pyridine (15) favored 4-substitution fairly strongly. The latter reagent was quite successful for the preparation of the 4-bromo-2-ester, although less so for the corresponding aldehyde. The only similar monobrominated pyrrole has been prepared by Ciamician (16) through the action of bromine in acetic acid on 2-acetylpyrrole, and later identified as the 4-bromo derivative by n.m.r. (17). The same compound has also been obtained by the action of the dioxane–bromine complex (18). It seems surprising that although some dibrominated product was isolated none of the 5-isomer was found. The contrast with the thiophene series, where bromination of the 2-aldehyde (19) and the 2-acid (20) using bromine produced the 5- but not the 4-bromo derivative, points up the selectivity of the bromination reaction.

It was found in general that nucleophilic substitution of the bromine in these compounds

was difficult. The displacement of bromine by cyanide in the ester series was not a satisfactory conversion. This is in agreement with results reported for thiophene derivatives (3). Attempts to replace the bromine with methoxyl by refluxing the monobromo-2-ester with sodium methoxide in methanol for 30 h were unsuccessful. It appears that much more drastic conditions would be necessary to make this conversion successful. The reaction takes place moderately well in the thiophene and furan series (4, 5).

It was found that the bromines could be removed from the ring by reduction. Catalytic hydrogenation was much more successful than zinc and acetic acid or other chemical means. The 5-bromine was removed more rapidly than the 4-bromine. It was thus possible to reduce the 4,5-dibromo compounds to a mixture in which the 4-bromo compound predominated. However, this seemed to have little preparative value since some complete reduction also took place. Bromine was less readily removed from the aldehydes than from the corresponding esters. Although the corresponding bromo-2-acids were obtained, from the ester and from the aldehyde, it was found that their purification was very difficult and they rapidly blackened. Various attempts to isolate the products of decarboxylation using a variety of conditions were all unsuccessful. These included dry distillation from a mixture with copper–bronze and from a mixture with soda–lime, as well as distillation from quinoline and copper powder.

EXPERIMENTAL

General

Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Infrared spectra were recorded by a Perkin–Elmer 237-B grating spectrophotometer using the potassium chloride disc technique (2 mg of sample in 200 mg KCl). Ultraviolet spectra were determined with a Beckman DK-2A recording spectrophotometer at a concentration of 10 mg per liter in ethanol (95%). Elemental analyses were determined by Alfred Bernhardt, Mülheim (Ruhr), Germany.

Analyses of reaction mixtures were carried out by means of gas–liquid partition chromatography using a Beckman GC-2A gas chromatograph, equipped with an 18 in. column (No. 70008) packed with Apiezon L on fire brick. For the pyrrole esters operation was at 220° using helium as carrier gas at 20 p.s.i.g. inlet pressure. Retention times established for pure compounds were: methyl 2-pyrrolecarboxylate, 0.9 min; 5-bromo derivative, 2.1 min; 4-bromo derivative, 3.5 min; 4,5-dibromo derivative, 6.5 min. For the pyrrole aldehydes operation was at 190° using helium as carrier gas at 20 p.s.i.g. inlet pressure. Retention times established for pure compounds were: 2-pyrrolecarboxaldehyde, 1.3 min; 5-bromo derivative, 3.3 min; 4-bromo derivative, 4.7 min; 4,5-dibromo derivative, 12.5 min.

Starting Materials

Methyl 2-pyrrolecarboxylate was prepared and purified as described in ref. 1. 2-Pyrrolecarboxaldehyde was prepared by the method of Silverstein, Ryskiewicz, and Willard (21).

General Procedure for Bromination with Bromine

In a 100 ml three-necked round bottom flask equipped with a sealed stirrer, a condenser, and a dropping funnel, was placed 0.004 mole of starting material along with 2–3 mg of iodine dissolved in 30 ml of carbon tetrachloride. A solution of bromine (0.004 mole) in 10 ml of carbon tetrachloride was added dropwise, with stirring. The mixture was neutralized with 20% sodium carbonate solution, the layers separated, and the aqueous layer extracted with ether. The combined organic layers were dried over sodium sulfate and the solvents were removed by flash evaporation. The residue was injected into the gas chromatograph in ether solution. The results of the analyses, together with conditions of time, temperature, and concentration are listed in Table I.

Isolation of Bromination Products

The solid material, after flash evaporation of solvents, was chromatographed on neutral alumina (Woelm, No. 1), following the progress of elution by means of gas chromatography. Homogeneous fractions were isolated, and the solids sublimed and recrystallized from petroleum pentanes to obtain purified products.

Methyl 4-bromo-2-pyrrolecarboxylate, m.p. 98–99°. Calcd. for $C_6H_6NO_2Br$: C, 35.32; H,2.96; N, 6.87; Br, 39.16. Found: C, 35.52; H, 2.93; N, 7.01; Br, 39.21. Methyl 5-bromo-2-pyrrolecarboxylate, m.p. 102–103°. Calcd. for $C_6H_6NO_2Br$: C, 35.32; H, 2.96; N, 6.87; Br, 39.16. Found: C, 35.15; H, 3.07; N, 6.55; Br 39.31. Methyl 4,5-dibromo-2-pyrrolecarboxylate, m.p. 158–159°. Calcd. for $C_6H_5NO_2Br_2$: C, 25.47; H, 1.78; N. 4.95; Br, 56.49. Found: C, 25.30; H, 1.65; N, 4.86; Br, 56.71. 4-Bromo-2-pyrrolecarboxaldehyde, m.p. 123–124°. Calcd. for C_5H_4NOBr: C, 34.51; H, 2.32; N, 8.05; Br, 45.93. Found: C, 34.68; H, 2.39; N, 7.87;

Br, 46.04. 5-Bromo-2-pyrrolecarboxaldehyde, m.p. 93–94°. Calcd. for C_5H_4NOBr: C, 34.51; H, 2.32; N, 8.05. Found: C, 34.67; H, 2.51; N, 7.80. 4,5-Dibromo-2-pyrrolecarboxaldehyde, m.p. 155–156°. Calcd. for $C_5H_3NOBr_2$: C, 23.75; H, 1.11; N, 5.54. Found: C, 23.66; H, 1.43; N, 5.71.

Bromination with Other Reagents

In each trial 0.004 mole of starting material was treated with 0.004 mole of the brominating reagent. The reaction time was usually judged on the basis of a color change. Working-up involved standard procedures for the removal of by-products, depending on the reagent. This was followed by flash evaporation of the solvent, and gas chromatographic analysis. The results are listed in Table II. (*a*) The bromination in carbon tetrachloride was carried out at 70° for 60 min using a small amount of iron powder as catalyst. (*b*) The bromination was carried out in carbon tetrachloride at room temperature for 120 min in the presence of an excess (0.008 mole) of anhydrous aluminium chloride. (*c*) The bromine–dioxane complex (22) was used in dioxane solution at 60° for 30 min. (*d*) Bromination was carried out at 60° in a solution of 30 ml glacial acetic acid containing 0.75 g sodium acetate. (*e*) N-Bromosuccinimide was used at the boiling point of the carbon tetrachloride solution and in the presence of about 0.1 g benzoyl peroxide. Reaction time was 90 min. (*f*) The bromonium ion was prepared by the action of bromine on silver perchlorate (0.012 mole) in aqueous perchloric acid solution (3 ml, 72%). The reaction proceeded at room temperature over 30 min. (*g*) Hypobromous acid solution (0.079 *N*) was prepared by the action of freshly prepared mercuric oxide on bromine in an excess of water (23). The reaction was carried out at room temperature in the presence of 72% perchloric acid (0.10 mole) over 30 min (13). (*h*) Pyridinium bromide perbromide was used in pyridine solution at room temperature over 1 h (15). (*i*) The sodium hypobromite solution was prepared by dissolving bromine in 40 ml 6 *N* aqueous sodium hydroxide. (*j*) The mixture of cupric bromide and starting material together with 0.0005 mole of lithium bromide was heated at 150° for 2 h in 25 ml of dimethylformamide (24).

Preparation of Brominated Acids and Their Esterification

(*a*) The brominated ester (0.008 mole) was refluxed with a mixture of 25 ml of 20% aqueous potassium hydroxide and 20 ml of methanol for 2 h. The methanol was removed under vacuum and unreacted ester extracted with ether. The aqueous layer was acidified with dilute hydrochloric acid and extracted with ether. After drying, the ether solution was evaporated and the crude solid was sublimed and recrystallized.

(*b*) The brominated aldehyde (0.0002 mole) in 2 ml of ethanol was added to a suspension of silver oxide (from 50 mg of silver nitrate, 5 ml of water, and 10 ml of 1 *N* sodium hydroxide solution). The mixture was shaken mechanically for 1 h at room temperature and filtered (25). The filtrate was acidified and extracted with ether. The extract was dried and the product was isolated by evaporation.

Products obtained by methods (*a*) and (*b*) were: 4-bromo-2-pyrrolecarboxylic acid, m.p. 155–165°; 5-bromo-2-pyrrolecarboxylic acid, which decomposed in air after a short time; 4,5-dibromo-2-pyrrolecarboxylic acid, m.p. 165–175°. All attempts to purify these compounds caused extensive decomposition.

The addition of an ethereal solution of diazomethane (26) to the ethereal solution obtained by method (*b*), followed by keeping overnight at room temperature converted the crude acids directly to the corresponding esters. The products were proved identical to those from direct bromination of the 2-ester by mixed melting points and comparison of infrared spectra.

Reductive Removal of Bromine

(*a*) A solution of methyl 4,5-dibromo-2-pyrrolecarboxylate (0.004 mole) in 30 ml of glacial acetic acid was refluxed gently while zinc dust (0.001 mole) was added slowly. After a further 3 h heating the solution was cooled, neutralized with base, and extracted with ether. Gas-chromatographic analysis of the dried extract indicated: methyl 2-pyrrolecarboxylate, trace; methyl 4-bromo-2-pyrrolecarboxylate, 5.9%; methyl 5-bromo-2-pyrrolecarboxylate, 2.1%; starting material, 92%.

(*b*) A solution of brominated ester or aldehyde (50 mg) was dissolved in 25 ml of glacial acetic acid containing 10 mg sodium acetate. After adding 20 mg of 5% palladium-on-charcoal catalyst the reaction mixture was shaken in a heavy-wall glass bottle under 3 atm of hydrogen at 60° for from 10 min to 2 h depending on the compound. After removal of the catalyst, neutralization, extraction, and drying, gas-chromatographic analysis showed quantitative removal of bromine.

(*c*) With the same starting materials the reductions were carried out at room temperature and pressure while agitating the reaction mixture with a magnetic stirrer. Again quantitative reduction was observed over times ranging from 15 min to 3 h.

Products were isolated from all these reductions and identified.

Replacement of Bromine with Cyanide

A mixture of the bromopyrrole ester (0.01 mole) and freshly prepared cuprous cyanide (0.015 mole) (27) in 50 ml of dimethyl sulfoxide was refluxed for 5 h. Most of the solvent was removed by vacuum distillation and the dark residue was washed with 30 ml of 20% aqueous ammonium chloride and extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate. After evaporation of the ether the nitrile was obtained by crystallization from petroleum pentanes and sublimation. Yields averaged about 20%. The products were: methyl 5-cyano-2-pyrrolecarboxylate, m.p. 165–166°. Calcd. for $C_7H_6O_2N_2$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.82; H, 4.11; N, 18.57. Methyl 4-cyano-2-pyrrolecarboxylate, m.p. 169–170°. Calcd. for $C_7H_6N_2O_2$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.96; H, 4.19; N, 18.71.

Formylation of Methyl 2-Pyrrolecarboxylate

Following the procedure of Silverstein *et al.* (21) methyl 2-pyrrolecarboxylate (0.04 mole) was formylated with 3.5 g of dimethylformamide and 7.0 g of phosphorus oxychloride in 25 ml of ethylene chloride. After working-up, the product was distilled at 120° and 5 mm giving a product which, after sublimation, melted at 92–93°. The undistilled residue was purified by recrystallization from pentane, and sublimation, to m.p. 121–122°. Over 90% of the ester was converted to products.

Identification of Formylated Pyrrole Esters

Each of the formyl-2-esters was oxidized with alkaline silver oxide following the procedure outlined above for the brominated aldehydes. Each crude acid in ether was then esterified by the addition of an ethereal solution of diazomethane. Yields were very good. From the formyl-2-ester, m.p. 92–93°, was obtained: methyl 2,4-pyrroledicarboxylate, m.p. 126–127°; λ_{max} 264 mμ (ϵ 13 700). (Reference 11 gives m.p. 126–127°; λ_{max} 267 mμ in aqueous solution.) Calcd. for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.97; H, 4.71; N, 9.21; From the formyl-2-ester, m.p. 121–122°, was obtained methyl 2,5-pyrroledicarboxylate, m.p. 128.5–129.5°; λ_{max} 274 mμ (ϵ 24 400). (Reference 11 gives m.p. 129–130°; λ_{max} 277 mμ in aqueous solution.) Calcd. for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.97; H, 4.72; N, 9.32.

Conversion of Formyl Derivatives to Cyano Derivatives

The now proven methyl 4-formyl-2-pyrrolecarboxylate (m.p. 92–93°) was converted to its oxime, m.p. 204–205°, and dehydrated with hot acetic anhydride (28) to the corresponding methyl 4-cyano-2-pyrrolecarboxylate. Similarly the 5-formyl-2-ester was converted by way of its oxime, m.p. 123–124°, to methyl 5-cyano-2-pyrrolecarboxylate. These compounds were then used to prove the structures of the same compounds obtained above by displacement of bromine by cyanide. Mixed melting points were undepressed and infrared spectra corresponded.

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