Reductive *C*-alkylation. II[1]

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Methylpyrrole carboxylic esters generally are reductively methylated at 25–45°. Some are also reductively alkylated by aliphatic aldehydes generally to give, for example, 2,3(or 2,4)-dimethyl-4(or 3)-alkyl-5-carbethoxypyrroles, using hydriodic acid or HCl/AcOH–Zn/Hg respectively. An analogous alkylation by glyoxylic acid gave 5-carbethoxyhemopyrrole-dicarboxylic ester. Using HI, paraldehyde at 100° gave diethyl derivatives of dimethylpyrroles, and aminoacetal at 35° converted 2,4-dimethyl-3-acetylpyrrole into its 5-(2-amino-ethyl)-derivative. Reductive alkylations have been most useful with pyrroles but HI converted 2-biphenylcarbaldehyde into fluorene.

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Introduction

In a further study of reductive *C*-alkylation, cf. (1), the most useful results have again been obtained with pyrroles. Attempts to methylate furans, thiophene, imidazole, and indoles have been unsuccessful, like those to ethylate benzene derivatives. However, hydriodic acid converted 2-biphenylcarbaldehyde or its acetal into fluorene.

Table 1 summarizes the pyrrole alkylations now carried out with various aldehydes and cyclopentanone using HI or HCl/AcOH–Zn/Hg. The products are coded in the table to conform to the numbers of the starting pyrroles but are distinguished by added decimal numbers; however recurring products retain their original designations. The methods of alkylation are indicated by letters A–F and *a-e*, which correspond to details in the Experimental. When the required pyrrole was obtained, no effort was made to improve the yield. The choice between methods A and B, as that between C and D, was arbitrary.

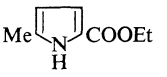
Tetramethylpyrrole (**2.1**) had been obtained from 2,4-dimethylpyrrole (**1**) and from some of its derivatives with paraformaldehyde and hydriodic acid at 100° (1). It has now been obtained in the same way from 2,3-dimethylpyrrole (**2**) from 2,5-dimethylpyrrole (**3**), from **10**, and from **13**. When paraldehyde was used instead of paraformaldehyde, the three dimethylpyrroles gave the corresponding dimethyl–diethylpyrroles (**1.1**, **2.2**, **3.1**). These latter alkylations are the first carried out with the more sensitive paraldehyde at 100°.

Reductive alkylations at 25–45°, retaining carbethoxy and acetyl groups, had been carried out on **9**, **11**, and particularly on **15** to show the variety of alkyl groups which could be introduced (1). These alkylations have been extended by the alkylation of **15** to **15.1** and to **15.2** with cyclopentanone and with aminoacetal, the latter introducing a ω-amino-ethyl group.

To find more useful applications of reductive alkylation, we studied that of pyrrole, 2-carbethoxypyrrole, and a representative series of methylpyrrole carboxylic esters at 25–45°, primarily with paraformaldehyde and paraldehyde. The results (Table 1) and earlier ones (1) separate the pyrroles into the following four groups. Presumably these define the applicability of the method to alkyl pyrrole carboxylic esters in general for, as will be reported later, the available homologues have behaved like the corresponding methyl derivatives.

(*i*) Not alkylated by paraformaldehyde: pyrrole and 2-carbethoxypyrrole,

(*ii*) Alkylated by paraformaldehyde but not by paraldehyde:



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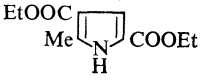

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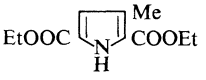

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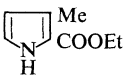
(*iii*) Alkylated by paraformaldehyde, paraldehyde and, presumably or in fact, higher aldehydes:



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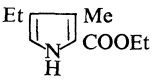

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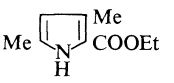

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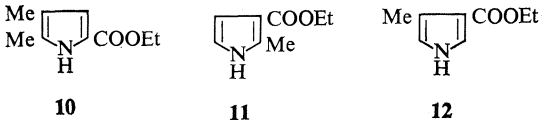
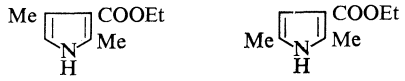
TABLE 1

Pyrroles and their alkylation products

Starting pyrrole	Alkylation method	Code	Substituents on pyrroles 2	3	4	5	% Yield	Melting point (°C) Found	Literature	Anal. Calcd. – Found C	H	N
		1	Me		Me							
1	B	**1.1**	"	Et	"	Et	56		(2*a*)	79.40 – 79.22	11.34 – 11.19	9.26 – 9.44
		2	Me	Me								
2	B	**2.1**	"	"	Me	Me	51	105–107	109–110(3)	77.99 – 77.81	10.64 – 10.32	11.37 – 11.45
2	B	**2.2**	"	"	Et	Et	48		(2*a*)	79.40 – 79.09	11.34 – 11.27	9.26 – 9.37
		3	Me			Me						
3	B	**2.1**	"	Me	Me	"	49	105–107				
3	B	**3.1**	"	Et	Et	"	46		(2*a*)	79.40 – 79.21	11.34 – 11.53	9.26 – 9.09
		4	COOEt			Me						
4	C*b*	**4.1**	"	Me	Me	"	50	127–129	128(2*b*)	66.27 – 66.42	8.34 – 8.40	7.73 – 7.89
		5	COOEt		COOEt	Me						
5	C($\frac{1}{2}$ h)*c*	**5.1**	"	Me	"	"	70	135	136(2*c*)	60.24 – 60.16	7.16 – 7.10	5.85 – 5.80
		6	COOEt	Me		COOEt						
6	C(45°, 3 h)*a*	**6.1**	"	"	Me	"	45	66–68	69–70(23)	60.24 – 59.93	7.16 – 7.21	5.85 – 6.06
		7	COOEt	Me								
7	C*b*	**4.1**	"	"	Me	Me	33	127–129		66.27 – 66.09	8.34 – 8.19	7.73 – 7.79
		8	COOEt	Me	Et							
8	C*b*	**8.1**	"	"	"	Me	53	91–92	95–96(2*d*)	67.66 – 67.69	8.78 – 8.72	7.17 – 7.19
8	C*b*	**8.2**	"	"	"	Et	64	71–73	73–74(4)	68.86 – 68.71	9.15 – 9.11	6.67 – 6.84
		9	COOEt	Me		Me						
9	F*b*	**9.1**	"	"	$CH_2CH_2CH_3$	"	48	99–99.5	98(5)	68.86 – 68.75	9.15 – 9.19	6.69 – 6.89
9	F*b*	**9.2**	"	"	$CHMe_2$	"	50	105–106.5		68.86 – 68.70	9.15 – 8.98	6.69 – 6.79
9	F*b*	**9.3**	"	"	$(CH_2)_3CH_3$	"	75	101–103	99(6)	69.92 – 69.84	9.48 – 9.37	6.27 – 6.37
9	F*c*	**9.4**	"	"	$(CH_2)_6CH_3$	"	51	47–49		72.41 – 72.60	10.26 – 10.11	5.28 – 5.23
9	F(25–30°, 1 h)*a*	**9.5**	"	"	$(CH_2)_{11}CH_3$	"	27	65–67		75.17 – 74.95	11.12 – 11.01	4.18 – 4.24
9	F(3 h)*d*	**9.6**	"	"	$(CH_2)_{17}CH_3$	"	40	76–78		77.27 – 77.11	11.77 – 11.71	3.34 – 3.27
		10	COOEt		Me	Me						
10	A	**2.1**	Me	Me	"	"	53	105–107				
10	C*b*	**4.1**	COOEt	Me	"	"	72	127–129		66.27 – 66.13	8.34 – 8.41	7.73 – 7.71
10	C*b*	**10.1**	"	Et	"	"	51	95–97	97(2*d*)	67.66 – 67.59	8.78 – 8.79	7.17 – 7.23
10	C(3 h)*d*	**10.2**	"	CH_2CHMe_2	"	"	45	109–111		69.92 – 70 23	9.48 – 9.79	6.27 – 6.27
10	C(3 h)*d*	**10.3**	"	$(CH_2)_6CH_3$	"	"	47	68–69		72.41 – 72.23	10.26 – 10.27	5.28 – 5.15
10	C(3 h)*b*	**10.4**	"	$(CH_2)_{11}CH_3$	"	"	35	70–71		75.17 – 75.08	11.12 – 11.04	4.18 – 4.30
10	C(3 h)*e*	**10.5**	"	$(CH_2)_{17}CH_3$	"	"	30	78–80		77.27 – 77.17	11.77 – 11.68	3.34 – 3.42
		12		COOEt	Me							
12	C*b*	**12.1**	Me	"	"	Me	70	103–105	104–105(2*e*)	66.27 – 66.11	8.34 – 8.18	7.73 – 7.65
12	C*e*	**12.2**	Et	"	"	Et	42	101–103		68.86 – 68.96	9.15 – 9.09	6.67 – 6.52
		13	Me	COOEt	Me							
13	A	**2.1**	"	Me	"	Me	53	105–107		77.99 – 77.96	10.64 – 10.43	11.37 – 11.47
13	C*b*	**12.1**	"	COOEt	"	Me	67	102–104		66.27 – 66.12	8.34 – 8.46	7.73 – 7.85
13	D*a*	**13.1**	"	"	"	Et	53	107–109	106–107(7)	67.66 – 67.31	8.78 – 8.72	7.17 – 7.08
		14	Me	COOEt		Me						
14	C*b*	**12.1**	"	"	Me	"	70	103–105		66.27 – 66.10	8.34 – 8.30	7.73 – 7.81
14	C*b*	**14.1**	"	"	Et	"	75	105–107	106–107(8)	67.66 – 67.54	8.78 – 8.69	7.17 – 7.28
14	C(1 h)*b*	**14.2**	"	"	$(CH_2)_4CH_3$	"	52	78–79		70.85 – 70.71	9.77 – 9.57	5.90 – 6.02
		15	Me	COMe	Me							
15	D*b*	**15.1**	"	"	"	$CH<(CH_2)_4$	95	167.5–168	164.5–165.5(9)	76.05 – 76.12	9.33 – 9.21	6.82 – 6.65
15	E	**15.2**	"	"	"	$CH_2CH_2NH_2$	29	106.5–107.5		66.63 – 66.51	8.95 – 8.89	15.54 – 15.62
		16	COOEt	CH_2CH_2COOEt		Me						
16	D*d*	**16.1**	"	"	Me	"	48	90.5–91.5	91(10)	62.90 – 63.06	7.92 – 8.03	5.24 – 5.19
16	D*c*	**16.2**	"	"	CH_2COOEt	"	75	66–66.5	66(11)	60.16 – 60.40	7.43 – 7.65	4.13 – 4.31
		17	COOEt	Me	Br	Me						
17	C*b*	**4.1**	"	"	Me	"	60	126–127		66.27 – 66.20	8.34 – 8.30	7.73 – 7.88

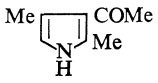


10 **11** **12**



13 **14**

(*iv*) Alkylated by aldehydes and ketones:



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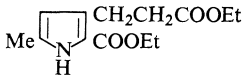
In the third group, the status of **7** is uncertain for its ethylation was not attempted. Some members of this group have been alkylated with higher aliphatic aldehydes to C-18 (cf. **9.1–9.6, 10.2–10.5, 14.2**) and, as no failures were encountered, the rest presumably could be. All that is known of their alkylation by ketones suggests that the results will be variable: **9** was alkylated to **9.2** by acetone but its alkylation by 2-butanone was incomplete. Alkylation by ketones will be less important because the alkyl groups in pyrroles from natural pigments are primary.

We normally used hydriodic acid, but hydrogen chloride in acetic acid with zinc amalgam was used in the alkylation of **9** by carbonyl compounds other than paraformaldehyde. Hydriodic acid was ineffective there and, in one case at least, gave the 3-(1-iodo-alkyl) derivative (1). There is no evidence that the zinc method is preferable in any other circumstances. It too failed in the ethylation of **4**, **5**, and **6** and, although an iodoalkyl derivative was again encountered in methylating **6** for only $\frac{1}{2}$ h using hydriodic acid, this was a transient intermediate.

Evidently the structural features making **9** more easily substituted than **10** (18) do not equally favor the reduction of its iodoalkyl derivatives with hydriodic acid. An analogous case is evident in the reduction of the methoxy-benzyl bromides by the same reagent, where the *m*-isomer is reduced fastest (12). As iodoacetic acid is reduced by hydriodic acid at room temperature (13), it was not surprising that **16**, though an analogue of **9**, was alkylated normally by glyoxylic acid and hydriodic acid.

The behavior of **4** with paraldehyde, in contrast to that of **9** and **10**, suggests that one factor limiting the generality of the method may be a difficulty in reducing complex intermediates from polydentate pyrroles at temperatures compatible with the retention of carbethoxy groups.

The more practical applications involved **5**, **9**, **10**, and **16**. Unfortunately, useful intermediates were not obtained from **5**. However, homologues of cryptopyrrole and hemopyrrole were obtained generally from **9** and **10** as 5-carbethoxy derivatives, and more complex hemopyrrole derivatives were obtained by alkylating **16** to **16.1** and **16.2** with paraformaldehyde or, as mentioned above, with glyoxylic acid.



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Finally, the displacement of halogen is illustrated by the methylation of 2,4-dimethyl-3-bromo-5-carbethoxypyrrole (**17**).

Experimental

Hydriodic acid (*d*, 1.94) and 50% hypophosphorus acid were used. The aldehydes were monomers except paraformaldehyde, paraldehyde, and stearaldehyde trimer. The sources of the starting pyrroles were as follows: **1**(2*f*); **2**(14); **3**, **5**, **10** (see below); **4**(15); **6**, **7**(16); **8**(2*g*); **9**(2*h*); **12**(17); **13**, **14**(2*i*); **15**(1); **16**(18); **17**(2*j*). Magnetic stirring was used. The m.p. are corrected. The nuclear magnetic resonance (n.m.r.) spectra of all the products were consistent with their assigned structures. The pyrroles gave positive Ehrlich reactions hot, and negative Beilstein tests for halogen.

2,5-Dimethylpyrrole (3)

Ammonium chloride (20 g) and ammonium carbonate (50 g) were dissolved in ammonium hydroxide (150 ml) by stirring at 35°. 2,5-Hexanedione (102.5 g) was added and the temperature rose to 60° over 5 min. The mixture was then heated and stirred for 10 min and the product (88%) was isolated as usual (19), b.p. 51.3–53.3°/6 mm.

2-Methyl-3,5-dicarbethoxypyrrole (5)

Phosgene (3 g) in toluene (15 ml) was added to 2-methyl-3-carbethoxypyrrole (4.59 g) in 20 ml of toluene and 3.63 g of dimethylaniline at room temperature. The mixture was allowed to stand overnight, then refluxed for 2 h. Dimethylaniline (3.63 g) in 20 ml of absolute ethanol was added at room temperature, the mixture was refluxed for 1 h, and the volatile material was removed in a rotary evaporator. The residue was added to 250 ml of 10% hydrochloric acid, and the precipitated solid was recrystallized from ethanol; yield, 70%; m.p. 129–131° (lit. (2*c*) 132°).

Anal. Calcd. for $C_{11}H_{15}O_4N$: C, 58.65; H, 6.71; N, 6.22. Found: C, 58.48; H, 6.42; N, 6.04.

*2,3-Dimethyl-5-carbethoxypyrrole (**10**)*

The carbethoxy group was introduced into 2,3-dimethylpyrrole exactly as into 2-methylpyrrole (15). The yield was 65%; m.p. 113–115° (lit. (*2h*) 114°).

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.55; H, 7.69; N, 8.49.

Methods of Alkylation Referred to in Table 1

A. The pyrrole (0.82 g) and paraformaldehyde (0.6 g) in 10 ml of acetic acid, 10 ml of hydriodic acid, and 2 ml of hypophosphorus acid were stirred for 3 h under nitrogen at 100°. The mixture was poured into water, made alkaline with ammonia, and extracted with ether. The ether was evaporated and the residue distilled (65°, 15 mm).

B. The pyrrole (2 g) and paraformaldehyde (1.2 g) in 50 ml of acetic acid, 50 ml of hydriodic acid, and 10 ml of hypophosphorus acid were treated as in method A. If paraldehyde (1.4 ml, an unintentional deficit) was used instead of paraformaldehyde, the product was distilled at ca. 50° (0.05 mm).

C. The pyrrole (4 mmoles) and 0.6 g of paraformaldehyde (or another aldehyde, for **10.4**, **10.5**, and **14.2** the theoretical amount, otherwise twice that) in 10 ml of acetic acid, 10 ml of hydriodic acid, and 2 ml of hypophosphorus acid were stirred at 25° (or as specified) for $2\frac{1}{2}$ h (or as specified). The solution (in the case of **5.1**, a suspension containing a labile and insoluble complex of this with iodine) was poured into water. The mixture was made alkaline with ammonia and the product was isolated by one of the following methods.

The solid was crystallized from (*a*) *n*-pentane, (*b*) ether – *n*-pentane, or (*c*) methanol.

The mixture was extracted with ether, the ether was evaporated, and the residue was distilled (1×10^{-4} mm) then crystallized from (*d*) *n*-pentane or (*e*) ether – *n*-pentane.

D. Hydriodic acid (10 ml) was stirred and cooled while 10 ml of acetic anhydride then 2 ml of hypophosphorus acid were added. The finely powdered pyrrole (4 mmoles) was added and stirred to solution, warming gently if necessary, then treated by one of the following methods.

(*a*) Paraldehyde (0.75 ml) was added and the solution was stirred for 5 min, decolorized with phosphonium iodide, and poured into 125 ml of ice-water. The cooled mixture was brought to p*H* 8 with ammonia and the solid was distilled (90–100°, 5×10^{-4} mm) then crystallized from *n*-hexane.

(*b*) Cyclopentanone (1.5 ml) was added in 3 portions over 45 min at 40°. After a further 30 min the solution was poured into ice-water and the solid was crystallized from *n*-hexane, from aqueous methanol, and again from *n*-hexane.

(*c*) Glyoxylic acid monohydrate (1.1 g) was added in 3 portions over 15 min at 40°. After a further 15 min the solution was evaporated (rotary, 25 then 35° bath, finally 0.5 mm). The residue was rubbed with 4 ml of water and left at 0° overnight. The solid was separated, washed with water (2 ml), dried, and warmed to solution in 5 ml of 7% hydrogen chloride in ethanol. After 6 h at 20° and some time at 0°, the product crystallized and more was obtained from the concentrated and cooled mother liquor. It was recrystallized from pentane.

(*d*) Paraformaldehyde (240 mg) was added, the solution was stirred 30 min, and the product was isolated as under (*c*).

E. Aminoacetaldehyde dimethyl acetal (0.75 ml) was dropped into a stirred solution of the pyrrole (548 mg) in 10 ml of hydriodic acid and 2 ml of hypophosphorus acid. The temperature rose to 50° then fell. After stirring for 4 h, finally at 35°, the mixture was evaporated in a shallow dish in a vacuum desiccator over KOH, finally at 0.1 mm. The residue was twice slurried and filtered with acetone. The clarified solution of the washed residue in water (5 ml) was made strongly alkaline with KOH, saturated with K_2CO_3, and extracted repeatedly with ether. The extract (125 ml) was boiled down, adding *n*-pentane toward the end to precipitate the product as pale yellow prisms.

Neut. Equiv. Calcd.: 180. Found: 182.

F. Acetic anhydride (20 ml) was stirred into 5 ml of cooled concentrated hydrochloric acid. The finely powdered pyrrole (4 mmoles) was dissolved in this and the carbonyl compound (8 mmoles) then added, followed by 10 g of zinc amalgam (20 mesh). The mixture was stirred at 20–25° (or as indicated) for 15 min (or as indicated), then decanted into ice-water. The product was isolated by one of the following methods.

The solid was distilled (1×10^{-4} mm) and either (*a*) distilled again or (*b*) crystallized from aqueous ethanol.

The mixture was extracted with ether, the washed and dried ether was evaporated, and the residue was either (*c*) distilled (100°, 1×10^{-4} mm) or (*d*) distilled (145–150°, 1×10^{-4} mm) then crystallized from pentane.

2-Biphenylcarbaldehyde Diethyl Acetal

An ethereal solution of the Grignard reagent from 2-iodobiphenyl and magnesium was treated with ethyl orthoformate, refluxed for 3 h, then worked up. The distilled product, which solidified at 0°, was drained on tile to give a crude product (ca. 80%) containing biphenyl. This was steam-distilled until about half had passed over, when the m.p. of the residue was constant and the vapor no longer smelt of biphenyl. The residue was distilled (ca. 85°, 1×10^{-3} mm) to give colorless prisms, m.p. 62–63°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.48; H, 7.84.

2-Biphenylcarbaldehyde (cf. 20–22)

The crude acetal (70 g) was hydrolyzed in 60 ml of water, 200 ml of acetic acid, and 10 ml of concentrated hydrochloric acid and the crude aldehyde, which resinified easily, was isolated and distilled, b.p. 148–151°/12 mm. Of this, 10 g was stirred for 2 days with saturated aqueous sodium metabisulfite (100 ml). The solid bisulfite complex was repeatedly washed with ether and with benzene, dissolved in water, and the p*H* of the solution was brought to 9. The aldehyde was isolated from this, using ether, as an oil (3.25 g) b.p. ca. 85°/0.1 mm, n_D^{26} 1.6200.

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.51; H, 5.40.

Fluorene

Hydriodic acid (10 ml) and 1 ml of hypophosphorus acid were stirred at 100° while 0.768 g of 2-biphenylcarbaldehyde (or 1.024 g of the acetal) in 5 ml of acetic acid were added. The mixture was stirred and slowly distilled

until the vapor reached 125° after 1 h. The combined distillate and residue were diluted with water and the product isolated using ether. It was sublimed (< 100°, 5×10^{-4} mm) and crystallized from methanol as colorless prisms (83%); Beilstein test for halogen was negative, m.p. 117.5–118° undepressed with authentic fluorene.

Anal. Calcd. for $C_{13}H_{10}$: C, 93.94; H, 6.06. Found: C, 93.67; H, 6.20.

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