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PYRROLE CHEMISTRY—IX*

A NEW SYNTHESIS OF 3-ACYLPYRROLES FROM 4-ACYL-2-PYRROLETHIOLCARBOXYLATES USING A CATALYTIC DECARBONYLATION REACTION

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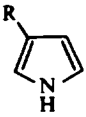
Abstract—The Friedel-Crafts acylation reaction of ethyl 2-pyrrolethiolcarboxylate gives good yields of 4-acylated products. The thiolcarboxylate group is replaced by hydrogen on treatment with W5 Raney Ni under carefully controlled conditions and provides a new route to 3-acylpyrroles. The removal of the 2-pyrrolethiolcarboxylate group by W5 Raney Ni appears to be quite general and using the reaction 3-acetyl-, 3-formyl-, 2-methyl-3-acetyl-, 2-methyl-3-formyl-, 2-acetyl- and 2-methyl-pyrrole have been prepared.

THE difficulties associated with the selective substitution of pyrrole in the 3-position[1] have led to the almost exclusive use of ring syntheses for the preparation of 3-substituted pyrroles.[2] Earlier papers in this series have reported on directive effects in electrophilic substitution reactions of pyrroles.[1] One of the aims has been to find new routes to the less accessible pyrroles, particularly those which can be obtained from pyrrole itself. In this paper a new route to 3-acylpyrroles from pyrrole is described.



I

R : a = —COOH
b = —COMe
c = —COPh
d = —CHO
e = —CN

Khan *et al.*[2] successfully modified the ring closure method devised by Rinkes[3] for the synthesis of 3-pyrrolecarboxylic acid (Ia) and 3-acetylpyrrole (Ib) to the synthesis of 3-benzoylpyrrole (Ic). However, the ring closure method could not be applied to the synthesis of 3-pyrrolecarbaldehyde (Id) and an alternative ring closure method had to be used for the preparation of 3-pyrrolecarbonitrile (Ie). 3-Pyrrolecarbaldehyde was finally obtained in very poor yield from the decarboxylation of 4-formyl-2-

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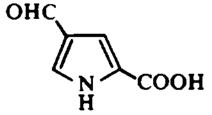
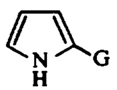
pyrrolecarboxylic acid (II), the hydrolysis product of ethyl 4-formyl-2-pyrrolecarboxylate obtained as a minor product from the formylation of ethhl 2-pyrrolecarboxylate.[2]

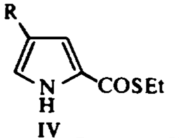

II


III

G: a = —CN
b = —COMe
c = —CHO
d = —COOMe

Although pyrrole gives predominantly 2-(5-)substituted products in electrophilic substitution reactions studies on the electrophilic substitution of pyrroles having various electron-withdrawing groups (–G) in the 2-position (III a–d) have shown that, as well as 2,5-disubstituted products, substantial amounts of 2,4-disubstituted products can be obtained. Friedel-Crafts alkylation and acylation gave particularly large amounts of 2,4-disubstitution and this was further enhanced when G was a powerfully electron withdrawing ("*meta*-directing") group, able to complex with the Friedel-Crafts catalyst.[1] Thus, to provide a synthesis of 3-substituted pyrroles a G group with good directing and protecting properties, and which can be readily removed, is required. None of the G groups (a–d) fulfill these requirements.

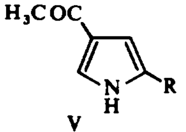
The conversion of substituted pyrrolethiolcarboxylates into the corresponding aldehydes, alcohols or methylpyrroles by reduction with Raney nickel has been described.[4] In view of the versatility of the thiolcarboxylate group we decided to investigate the substitution reactions of ethyl 2-pyrrolethiolcarboxylate (IVa) and the action of Raney Ni catalysts on the products so obtained. In the course of this work we found that, not only could the thiolcarboxylate (—COSEt) undergo the changes mentioned above, but it could also be replaced by hydrogen (—H) through the action of a suitable Raney Ni catalyst. The ethyl 2-pyrrolethiolcarboxylate closely resembles ethyl 2-pyrrolecarboxylate in electrophilic substitution reactions. Friedel-Crafts acylation gives almost exclusively 2,4-disubstituted products which can be converted by Raney nickel into 3-acylpyrroles.


IV

R: a = —H
b = —COMe
c = —CHO

Ethyl 2-pyrrolethiolcarboxylate (IVa) was readily obtained from the pyrrole Grignard reagent and ethyl chlorothiolformate. (The yield from this reaction was much better than that obtained from the analogous reaction between pyrrole Grignard reagent and ethyl chloroformate in the preparation of ethyl 2-pyrrolecarboxylate).[1b] The thiolester was then converted to ethyl 4-acetyl-2-pyrrolethiolcarboxylate (IVb) in a Friedel-Crafts reaction similar to those used for the preparation of ethyl 4-acetyl-2-pyrrolecarboxylate.

The 4-acetyl-2-pyrrolethiolcarboxylate (IVb) was refluxed in acetone with fresh W5 Raney Ni[5] to give 3-acetylpyrrole (Ib) in 79% yield. This represents a yield of ~20% from pyrrole. Earlier syntheses which used pyrrole as starting material obtained yields of only about 5%.[6, 1b] The reaction is straightforward and the products normally crystallise after the nickel has been removed and the solvent distilled off.



V

R: a = —CHO
b = —CH$_2$OH
c = —Me

By-products formed in the reaction in trace amounts were 4-acetyl-2-pyrrolecarbaldehyde (Va), 4-acetyl-2-hydroxymethylpyrrole (Vb), and 4-acetyl-2-methyl pyrrole (Vc). The first compound (Va) could be obtained as the major product by using deactivated Raney Ni under conditions similar to those reported earlier for the synthesis of aldehydes from pyrrole thiolesters.[4] Hydrogenation under pressure using a deactivated Raney nickel catalyst gave almost pure 4-acetyl-2-hydroxymethylpyrrole (Vb). Although PMR spectra indicated the presence of 4-acetyl-2-methylpyrrole (Vc) it was not easily obtained by this route due to very heavy contamination with the other possible reaction products.

The extension of the above synthesis of 3-acetylpyrrole (Ib) to the preparation of 3-pyrrolecarbaldehyde (Id) was hampered by the lack of an efficient route to ethyl 4-formyl-2-pyrrolethiolcarboxylate (IVc). The problems involved here were the same as those found by Khan *et al.* for the preparation of ethyl 4-formyl-2-pyrrolecarboxylate from ethyl 2-pyrrolecarboxylate.[2] The most successful synthesis available, using the Vilsmeier reaction, gave mostly the 5-formylated product.[2] In earlier work on the perchloric acid catalysed acetylation of methyl 2-pyrrolecarboxylate almost equal amounts of the 4- and 5-acetylation products were obtained,[7] whereas the Friedel-Crafts acetylation gave almost exclusively 4-substitution.[1b] These results suggested that a Friedel-Crafts formylation reaction would give predominantly 4-formyl-2-pyrrolethiolcarboxylate.

Attempted formylation of ethyl 2-pyrrolethiolcarboxylate with formamide[8] or ethyl orthoformate[8] in the presence of aluminium chloride failed, but under carefully chosen conditions formylation with dichloromethyl methyl ether[9] and aluminium chloride was successful and gave the 4-formyl isomer contaminated with only a trace of the 5-isomer. When the formylation was carried out in pure carbon disulphide or dichloromethane solution the yield was poor and a large amount of fluorescent material was formed (not identified). However, the addition of a small amount of nitromethane to the solvent circumvented the problem and raised the yield to over 50%. The nitromethane acts as a moderating agent, complexing with, and decreasing the activity of the aluminium chloride catalyst. The deactivation of the catalyst did not appear to affect the selectivity of the reaction. (Methyl 4-formyl-2-pyrrolecarboxylate can be prepared from methyl 2-pyrrolecarboxylate using the same method).

Ethyl 4-formyl-2-pyrrolethiolcarboxylate (IVc) when treated with slightly deactivated W5 Raney Ni in refluxing acetone gave 3-formylpyrrole (Id) (52% or about 15% from pyrrole). Again, by-products may be formed in the reaction if the catalyst used is not fresh or was not prepared correctly. 2,4-Pyrroledicarbaldehyde was isolated from several reactions (an expected by-product) and the amount increased as the activity of the Raney Ni decreased. The product distribution was sensitive to the reaction conditions due to the labile 3-formyl group. Fresh undeactivated W5 Raney Ni in refluxing ethanol or acetone converted the 4-formyl-2-pyrrolethiolcarboxylate into pyrrole itself.

The preparation of 2-substituted pyrroles, though less important from the preparative point of view, can also be carried out by the same method. Ethyl 5-acetyl-2-pyrrolethiolcarboxylate gave 2-acetylpyrrole and ethyl 2-methyl-5-pyrrolethiolcarboxylate gave 2-methylpyrrole. Methyl 2-methyl-3-acetyl-5-pyrrolethiolcarboxylate and methyl 2-methyl-3-formyl-5-pyrrolethiolcarboxylate gave 2-methyl-3-acetylpyrrole and 2-methyl-3-pyrrolecarbaldehyde respectively.

Spectral properties of some of the compounds used in this work are recorded in Tables 1 and 2.

TABLE 1. PMR SPECTRA OF SOME PYRROLES

Pyrrole	2H	3H	4H	5H	C$\underline{H}$O	J Hz
3-$COCH_3$[1b]	2·59		3·32	3·23		$J_{2,5}$ 1·90, $J_{2,4}$ 1·60, $J_{4,5}$ 2·98
2-CH_3, 3-$COCH_3$			3·43	3·43		
3-CHO	2·53		3·33	3·16	0·18	
2-CH_3, 3-CHO			3·40	3·30	0·08	$J_{1,4}$ and $J_{1,5}$ 3, $J_{4,5}$ 3·2
2-CHO, 4-CHO*		2·54		2·03	0·32 0·10	$J_{2,5CHO}$ 1, $J_{3,5}$ 1·4
2-$COSC_2H_5$, 4-CHO		2·59		2·34	0·13	$J_{1,3}$ 2·5, $J_{1,5}$ 3·4, $J_{3,5}$ 1·5
2-$COSC_2H_5$, 4-$COCH_3$		2·61		2·38		$J_{1,3}$ 2·5, $J_{1,5}$ 3·4, $J_{3,5}$ 1·6
2-$COSC_2H_5$, 5–$COCH_3$		(3·10, 3·15)				$J_{1,3}$ and $J_{1,4}$ 2·6, $J_{3,4}$ 4·2
2-$COSC_2H_5$		3·02	3·76	3·02		
c.f. 2-$COOCH_3$[1c]		3·02	3·70	3·02		
2-CH_2OH, 4-$COCH_3$ †	5·49	3·43		2·33		$J_{3,5}$ 1·7

* In acetone.

† In D_2O. The 2H resonance refers to the methylene protons.

A number of reactions which may be related to those described above have been reported but no attempt appears to have been made to apply them to the synthesis of pyrroles.[10–13] Catalytic decarbonylation reactions are well known and some are used industrially (eg. the conversion of 2-furaldehyde to furan).[12,13] Benzaldehyde loses carbon monoxide when refluxed with a small amount of palladised charcoal to give benzene.[13] The removal of the 2-thiolcarboxylate group from pyrroles by Raney Ni requires relatively mild conditions (most of the decarbonylation reactions require high temperatures)[10–13] and although the reactions were carried out in refluxing acetone they also took place at room temperature, though more slowly. Since it is known that the thiolcarboxylate group can be converted by Raney Ni

TABLE 2. IR AND UV SPECTRA

Pyrrole	ν_{max} cm^{-1}*			ε			νC=O cm^{-1}	
2-Me 3-COCH$_3$	35,800	41,000	48,600	6020	8110	21,500	1639	1624
3-CHO	$\underline{37{,}500}$	40,500	49,100	$\underline{7330}$	8880	11,130	1647	
2-Me 3-CHO	35,200	40,200	48,800	6590	9400	11,170	1638	
2-CHO 4-CHO	34,400	42,600		14,800	18,320		1644	1669
2-COSEt 4-CHO	33,500	37,100 38,300	43,900	16,220	8260 7960	18,960	1632	1643
2-COSEt 4-COCH$_3$	33,640	37,000 38,000	43,800	18,830	13,730 8060	23,020	1622	1662
2-COSEt 5-COCH$_3$	31,800	42,400 $\underline{43{,}500}$	50,000	29,830	12,140 $\underline{10{,}160}$	6890		
2-COSEt	33,450	41,800		18,540	5290		1617 (liq. film)	
2-CH$_2$OH 4-COCH$_3$	36,500	40,750	47,570 $\underline{47{,}000}$	5500	8550	16,010 $\underline{14{,}640}$	1635	1650

* Figures underlined refer to inflections.

into other groups it is not directly obvious at what stage replacement by hydrogen takes place. We are at present investigating the mechanism, scope and extensions to the reaction.

EXPERIMENTAL

M.ps were taken on a Fisher-Johns m.p. block, and are uncorrected.

IR spectra were recorded on a Perkin-Elmer 237B spectrophotometer by the KCl disc technique.[1b] UV spectra were determined in 95% EtOH with a Unicam SP800 spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU 6E instrument.

The PMR spectra were determined on a Varian A-60 spectrometer at 60 MHz. The chemical shifts are in ppm from TMS as an internal standard in CDCl$_3$ unless specified otherwise, and are recorded on the τ scale.

Elemental analyses were determined by Alfred Bernhardt, Mülheim (Ruhr), Germany.

Petroleum refers to the fraction b.p. 60–80° unless otherwise stated.

Ethyl 2-pyrrolethiolcarboxylate (IVa). Ethyl chlorothiolformate (12·5 g, 0·1 mole) in ether (15 ml) was added dropwise to a cold stirred soln of the pyrrole Grignard reagent[1b] (0·2 mole) in ether (100 ml). An exothermic reaction took place and the mixture eventually began to reflux. The mixture was stirred for a further 1 hr and then allowed to stand overnight, after which it was carefully hydrolysed with 10% NH$_4$Cl aq. The aqueous layer was separated from the organic layer and extracted with ether. The combined organic layers were washed with water, dried, and the ether was evaporated. The residue was fractionally distilled under reduced press. The low boiling material was mostly unchanged pyrrole (2·8 g) but the fraction b.p. 140–143°/14 mm was *ethyl 2-pyrrolethiolcarboxylate* (9·5 g) as a colourless oil which crystallized on cooling in ice. The product was recrystallized from an ether/petroleum mixture by cooling the soln in a solid CO$_2$/Me$_2$CO mixture, as needles (8·7 g, 56%), m.p. 29–29·5°. (Found: C, 54·57; H, 5·69; S, 20·95. C$_7$H$_9$NOS requires: C, 54·19; H, 5·85; S, 20·62%), M (mass spec) 155.

The pot residue from the distillation was mostly the known 2-pyrryl 2′-pyrryl ketone, m.p. 160–161° (lit.[1b] 160–161°). More vigorous reaction conditions increased the yield of the dipyrryl ketone.

Hydrolysis of the thiolester with aqueous methanolic KOH followed by acidification gave 2-pyrrolecarboxylic acid,[14] m.p. 207–208° (lit.[14] 207–208°).

Ethyl 4-acetyl-2-pyrrolethiolcarboxylate (IVb). Anhyd AlCl$_3$ (27·6 g, 0·207 moles) was suspended in CH$_2$Cl$_2$ (60 ml). The mixture was cooled and ethyl 2-pyrrolethiolcarboxylate (10 g, 0·065 moles) in CH$_2$Cl$_2$ (35 ml) was carefully added to the stirred mixture. The flask was then immersed in an oil bath maintained at 50° and Ac$_2$O (7·1 g, 0·069 moles) in CH$_2$Cl$_2$ (25 ml) was added dropwise. The mixture was stirred overnight and then poured into a 2N HCl/ice mixture (400 ml). The aqueous layer was separated and extracted with CH_2Cl_2. The extracts were combined with the organic layer, washed with water, 5% $NaHCO_3$aq, with water, and then dried ($MgSO_4$). The solvent was removed and the residue recrystallized from benzene/petroleum to give *ethyl 4-acetyl-2-pyrrolethiolcarboxylate* (6·93 g, 54%), m.p. 109–112°. Sublimation (110°/0·1 mm) gave the pure product m.p. 117–117·5°. (Found: C, 54·34; H, 5·40; S, 16·30. $C_9H_{11}NO_2S$ requires: C, 54·81; H, 5·62; S, 16·25%), M (mass spec.) 197.

Ethyl 4-formyl-2-pyrrolethiolcarboxylate (IVc). Under N_2 nitromethane (6 ml) in CH_2Cl_2 (50 ml) was added to a soln of ethyl 2-pyrrolethiolcarboxylate (5 g) in CH_2Cl_2 (50 ml). The stirred mixture was cooled in an ice bath and $AlCl_3$ (10 g) was added, followed by dichloromethyl methyl ether (5 g) in CH_2Cl_2 (50 ml). The mixture was stirred in an ice bath for 90 min and then poured onto ice. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The organic layer and the extracts were combined and washed with water, $NaHCO_3$aq, water and finally dried ($MgSO_4$), the solvent was removed and the brown oily residue was extracted repeatedly with boiling petroleum (b.p. 100–115°). The *product* crystallized from the petroleum as brownish needles, m.p. 111–112°, (3·16 g, 54%). The material was sublimed (120°/0·5 mm) to give needles of the same m.p. (Found: C, 52·48; H, 5·12; N, 7·57. $C_8H_9NO_2S$ requires: C, 52·45; H, 4·92; N, 7·65%).

3-*Acetylpyrrole* (Ib). Ethyl 4-acetyl-2-pyrrolethiolcarboxylate (250 mg) was dissolved in acetone (20 ml) and W5 Raney Ni[5] (~2 g) was added followed by acetone (20 ml). The mixture was then stirred under reflux for 30 min, cooled and filtered through a "Celite" pad to remove the Ni catalyst (care is required to ensure that the Ni does not dry out as the material is still highly pyrophoric). The Ni was washed several times with acetone and the filtrate and washing were combined. The acetone was removed leaving an oily residue which crystallized rapidly on cooling (149 mg). The product was recrystallized from $CHCl_3$/petroleum mixture, (109 mg, 79%), m.p. 114–115° (lit.[16] m.p. 115–116°). The mixture m.p. with authentic material was not depressed and their spectral properties were identical. Old specimens of Raney Ni gave products which contained some Va and Vb. These products were isolated by fractional crystallization and were identified by comparison with authentic specimens. PMR spectra of the crude reaction product indicated that Vc was also present in small amounts but it was not isolated pure. A synthesis of the latter compound by an alternative route will be reported later.

3-*Pyrrolecarbaldehyde* (Id). W5 Raney Ni[5] (4 g) was added to acetone (40 ml) and stirred at room temp for 15 min. Ethyl 4-formyl-2-pyrrolethiolcarboxylate (500 mg) was dissolved in acetone (40 ml) was added to the mixture which was then stirred for a further 30 min under reflux. The mixture was then cooled and filtered through a 'Celite' pad to remove the Ni catalyst, which was washed several times with acetone to remove trapped products. The acetone was removed and the oily residue was chromatographed on neutral alumina (Fluka, Type 507C neutral). A 1:1 mixture of ether in petroleum gave 3-pyrrolecarbaldehyde which was recrystallized from CCl_4/petroleum, (136 mg, 52%), m.p. 63–63·5° (lit.[2] m.p. 64°). Later fractions from the column contained a small amount of *2,4-pyrroledicarbaldehyde*, m.p. 151·5–152°. (Found: C, 58·68; H, 4·26; N, 11·53. $C_6H_5NO_2$ requires: C, 58·53; H, 4·09; N, 11·38%), M (mass spec) 123.

4-*Acetyl-2-hydroxymethylpyrrole* (Vb). W5 Raney Ni[5] (~8 g) was deactivated by stirring with acetone (80 ml) at room temp for 30 min. The Raney Ni was washed free of acetone with abs EtOH and transferred to a hydrogenation vessel under EtOH (80 ml). Ethyl 4-acetyl-2-pyrrolethiolcarboxylate (1 g) was added and the soln was hydrogenated (30 lb press) for 3 hr. The Raney Ni was removed by filtration through a "Celite" pad and the solvent was evaporated. The residue (584 mg) crystallized rapidly and was recrystallized from acetone and sublimed (115°/0·1 mm) to give pure *4-acetyl-2-hydroxymethylpyrrole*, (362 mg, 52%), m.p. 128°.* (Found: C, 60·53; H, 6·62; N, 10·04. $C_7H_9NO_2$ requires: C, 60·42; H, 6·52; N, 10·07%), M (mass spec) 139.

Methyl 2-methyl-3-acetyl-5-pyrrolethiolcarboxylate. The pyrrole was obtained from the acetylation of 2-methyl-5-pyrrolethiolcarboxylate with an AcOH/Ac_2O mixture catalysed by perchloric acid according to the method described.[4] The *product* was recrystallized from $CHCl_3$/petroleum, m.p. 182–183°. (Found: N, 7·27. $C_9H_{11}NO_2S$ requires: N, 7·10%), M (mass spec) 197.

2-*Methyl-3-acetylpyrrole*. Methyl 2-methyl-3-acetylpyrrole-5-thiolcarboxylate was treated with W5 Raney Ni as in the prep of 3-acetylpyrrole (above). The 2-methyl-3-acetylpyrrole (83%) was recrystallized

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* Lit. m.p. 90·5–91° was reported for the natural product Verrucarin E which was thought to be Vb [E. Fetz and Ch. Tamm, *Helv. Chim. Acta* 49, 349 (1966)]. Professor Tamm has informed us that the structure for Verrucarin E was incorrectly assigned, and that a revised structure is to be published.

from an ether/petroleum mixture, m.p. 86–87° (lit.[15] 75°). (Found: N, 11·44. Calc. for C_7H_9NO N, 11·37%), M (mass spec) 123.

2-Methyl-3-pyrrolecarbaldehyde. Methyl 2-methyl-3-formyl-5-pyrrolethiolcarboxylate[4] was treated with W5 Raney Ni as in the prep of 3-pyrrolecarbaldehyde (above). The *2-methyl-3-pyrrolecarbaldehyde* was recrystallized from petroleum, (50%), m.p. 121·5–122°. (Found: C, 66·26; H, 6·41; N, 13·04. C_6H_7NO requires: C, 66·03; H, 6·47; N, 12·84%), M (mass spec) 109.

Ethyl 5-acetyl-2-pyrrolethiolcarboxylate. Perchloric acid catalysed acetylation[4] of ethyl 2-pyrrolethiolcarboxylate gave a mixture of almost equal parts of the 4- and the 5-acetylated thiolester. Extraction of the crude reaction product with petroleum gave a soln of almost pure 5-acetylated product and a residue of the 4-acetylated product. Fractional crystallization of the partially separated isomers from pure samples of each. *Ethyl 5-acetyl-2-pyrrolethiolcarboxylate* had m.p. 70–71° (from petroleum). (Found: C, 54·92; H, 5·72; N, 7·00. $C_9H_{11}NO_2S$ requires: C, 54·81; H, 5·63; N, 7·10%).

2-Acetylpyrrole. Using the same method as described above for the synthesis of 3-acetylpyrrole (above), W5 Raney Ni converted ethyl 5-acetyl-2-pyrrolethiolcarboxylate into 2-acetylpyrrole (68%), m.p. 86–87° (lit.[1c] 88–89°). Mixture m.p. with an authentic sample was not depressed and the infrared spectra were superimposable.

2-Methylpyrrole. As in the preceeding experiment ethyl 2-methyl-2-pyrrolethiolcarboxylate was converted to 2-methyl pyrrole. The crude 2-methylpyrrole was treated with phenyl isothiocyanate and isolated as 5-methyl-2-pyrrolethiocarbanilide,[16] m.p. 105–106° (lit.[16] 109·5–111°), mixture m.p. with an authentic specimen 106–107°.

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