81. *Addition Reactions of Heterocyclic Compounds. Part VIII.** *Methyl Pyrrole-1-carboxylate and Dimethyl Acetylenedicarboxylate.*

By R. M. ACHESON and J. M. VERNON.

Methyl pyrrole-1-carboxylate with dimethyl acetylenedicarboxylate gave acetylene and trimethyl pyrrole-1,3,4-tricarboxylate, which was degraded to dimethyl pyrrole-3,4-dicarboxylate.

THE presence of an alkoxycarbonyl substituent at position 1 of the pyrrole nucleus inhibits the conjugation of the nitrogen p_π-electron pair with the π electrons of the double bonds of the ring. This reduces the susceptibility of the other ring positions to electrophilic attack. Ethyl pyrrole-1-carboxylate does not react with 2,4,6-trinitrobenzenediazonium sulphate, although many other pyrroles, including some pyrrole-2- and -3-carboxylic esters, are substituted by the less reactive *p*-nitrobenzenediazonium cation.[1]

The withdrawal of the π electrons from nitrogen by the alkoxycarbonyl group increases the aliphatic character of the ring diene system. Thus ethyl pyrrole-1-carboxylate is hydrogenated very much more easily than pyrrole itself,[2] and the hydrogenation of pyrrole

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* Part VII, *Proc. Chem. Soc.*, 1960, 281.

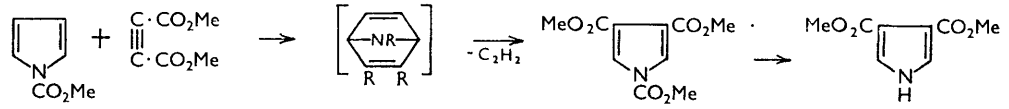
[1] Treibs and Fritz, *Annalen*, 1958, **611**, 162.

[2] Signaigo and Adkins, *J. Amer. Chem. Soc.*, 1936, **58**, 709.

is facilitated by acids.[3] In view of this it seemed interesting to discover whether 1-alkoxycarbonylpyrroles displayed any reactivity to dienophiles, especially since no Diels–Alder addition to such systems has been attempted.

When equimolecular proportions of methyl pyrrole-1-carboxylate and dimethyl acetylenedicarboxylate were allowed to react at room temperature a yellow colour developed, but evaporation gave only a tar smelling strongly of the acetylenic ester. When dimethyl acetylenedicarboxylate was added to this pyrrole at its boiling point there was an obvious darkening and a rise in temperature. Acetylene was evolved, and the tarry product afforded chromatographically a colourless substance, $C_{10}H_{11}NO_6$, containing three methoxyl groups.

This compound is trimethyl pyrrole-1,3,4-tricarboxylate (II) and is probably formed by elimination of acetylene from the hypothetical adduct (I); attempts to isolate this intermediate after reaction at intermediate temperatures in boiling benzene or xylene gave only tars. An adduct corresponding to (I) has been obtained from 1-benzylpyrrole and acetylenedicarboxylic acid; its dihydro-derivative decomposes to ethylene and 1-benzylpyrrole-3,4-dicarboxylic acid in hot aqueous sodium carbonate.[4]



(I; R = CO_2Me) (II) (III)

Degradative evidence supporting structure (II) has been obtained. Saponification followed by acidification precipitated a potassium salt of a carboxylic acid, which gave a dimethyl ester (III), $C_8H_9NO_4$. The same dimethyl ester was obtained directly by treatment of the triester (II) with cold methanolic alkali. It gave a positive Ehrlich reaction on heating, and its melting point agreed with that reported for dimethyl pyrrole-3,4-dicarboxylate.[5] The ultraviolet absorption spectrum of the triester (II) in methanol ($\lambda_{max.}$ 2500 Å; ε 7200) resembled the spectra of other pyrrolecarboxylic esters.[6] The degradation product (III) had a similar ultraviolet absorption spectrum, with a single maximum at 2500 Å; diethyl pyrrole-3,4-dicarboxylate has an absorption maximum at 2500 Å.[6]

EXPERIMENTAL

Methyl Pyrrole-1-*carboxylate*.—Freshly distilled pyrrole (27 g.) was converted into the potassium derivative by the method of Clemo and Ramage,[7] with potassium (16 g.). Methyl chloroformate (37 g.) in ether was added dropwise to the potassiopyrrole suspended in absolute ether (200 ml.), and cooled in water. After 30 min. at room temperature, the mixture was filtered. The filtrate and ethereal washings on distillation gave *methyl pyrrole*-1-*carboxylate* (43 g., 84%), b. p. 168—170° (Found: C, 57·2; H, 5·5; N, 11·1. $C_6H_7NO_2$ requires C, 57·6; H, 5·6; N, 11·2%). This ester with aqueous ammonia (*d* 0·880) at 100° gave, in 3 hr., pyrrole-1-carboxyamide, plates, m. p. 163° (lit.,[8] 166°).

Trimethyl Pyrrole-1,3,4-*tricarboxylate* (II).—Dimethyl acetylenedicarboxylate (14·2 g.) was added gradually to methyl pyrrole-1-carboxylate (12·5 g.) at its b. p. (170°). The internal temperature rose to 200°, where it was held for 1 hr. A slow stream of dry nitrogen admitted above the vapours condensing in the reflux condenser during this time swept out copious quantities of acetylene, which were absorbed in ammoniacal cuprous chloride solution, with precipitation of cuprous acetylide. When the mixture was left overnight, crystals appeared admixed with tar. This mixture, in a little benzene, was chromatographed on a 50 cm. alumina

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[3] Treibs and Kolm, *Annalen*, 1957, **606**, 166.

[4] Mandell and Blanchard, *J. Amer. Chem. Soc.*, 1957, **79**, 6198.

[5] Nicolaus and Mangoni, *Gazzetta*, 1956, **86**, 358.

[6] Scrocco and Nicolaus, *Atti Acad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1957, **22**, 500.

[7] Clemo and Ramage, *J.*, 1931, 49.

[8] Tschelinzeff and Maxoroff, *Ber.*, 1927, **60**, 194.

column (Spence grade H; deactivated with 5% of its weight of 10% aqueous acetic acid) prepared in light petroleum (b. p. 40—60°). Elution with light petroleum–benzene (1 : 1) gave the *triester* (10 g., 40%). Three recrystallisations from methanol afforded colourless crystals, m. p. 69° (Found: C, 49·9; H, 4·7; N, 6·0; OMe, 38·1%; *M*, 245. $C_{10}H_{11}NO_6$ requires C, 49·8; H, 4·6; N, 5·8; 3OMe, 38·6%; *M*, 241). In paraffin paste this showed maxima at 5·65, 5·70, and 5·80 μ in the carbonyl region.

Dimethyl Pyrrole-3,4-*dicarboxylate* (III).—(i) Potassium hydroxide (0·5 g.) in methanol (10 ml.) was added to trimethyl pyrrole-1,3,4-tricarboxylate (1·0 g.) in methanol (10 ml.). After 4 hr. with occasional shaking the precipitate was collected (0·7 g., 92%). Recrystallisation from a large volume of xylene gave the diester as needles, m. p. 244°.

(ii) Trimethyl pyrrole-1,3,4-tricarboxylate (1·0 g.) was heated under reflux with potassium hydroxide (1·5 g.) in methanol (10 ml.). After 24 hr. the solvent was evaporated, and the residue dissolved in water. Addition of concentrated hydrochloric acid caused effervescence, and precipitation of a colourless solid (0·5 g.), which was collected, washed, and dried. This product was infusible; it charred and left a residue when strongly heated. The product (0·3 g.) was dissolved in absolute methanol (50 ml.), saturated with dry hydrogen chloride, and left for 6 hr. The solution was evaporated to dryness and the solid residue (0·2 g.) was washed with aqueous sodium hydrogen carbonate and water, and dried. It recrystallised from methanol, giving the diester (III) as colourless prisms, m. p. 245° (lit.,[5] 245—246°; mixed with the product of the previous experiment, m. p. 244°) (Found: C, 52·8; H, 5·2; N, 7·6. Calc. for $C_8H_9NO_4$: C, 52·5; H, 5·0; N, 7·7%). In paraffin paste this showed one maximum, at 5·80 μ, in the carbonyl region, and N–H absorption at 3·10 μ.

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