

705. *Synthesis of Heterocyclic Compounds from  $\delta$ -Unsaturated 1 : 3-Diketo-esters.*

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Ethyl 6-*o*-methoxyphenyl-, 6-*p*-dimethylaminophenyl-, and 6-2'-furyl-2 : 4-dioxohex-5-enoates (II) have been synthesised; the known methyl and ethyl esters of this series were interconverted by alcoholysis.

Six of these esters were converted into 2 : 6-disubstituted 4-pyrones (V) on bromination, and dehydrobromination with potassium acetate. They were converted into 1-phenyl-5-styrylpyrazole-3-carboxylic esters (VI), the structures of which were determined by ozonolysis, decarboxylation, and hydrolysis to 1-phenylpyrazole-3-carboxylic acid. 3 : 5-Disubstituted *iso*-oxazoles (X) have also been prepared.

SYNTHESES and properties of  $\delta$ -unsaturated 1 : 3-diketo-esters have attracted the attention of various chemists.<sup>1</sup> The aromatic prototype, ethyl 2 : 4-dioxo-6-phenylhex-5-enoate (II; R = Et, R' = Ph) was first prepared by Schiff and Gigli<sup>2</sup> and later by Ruhemann.<sup>3</sup> Similarly, Ryan and Algar,<sup>4</sup> and Ryan and Plunkett,<sup>5</sup> prepared other hexenoates by the action of sodium on methyl oxalate and substituted methyl styryl ketones (I).

The present investigation involves the synthesis of ethyl 6-*o*-methoxyphenyl-, 6-*p*-dimethylaminophenyl-, and 6-2'-furyl-2 : 4-dioxohex-5-enoates (II) as well as interconversion of the methyl and ethyl esters by alcoholysis. These esters were obtained as described in the Experimental section in good yields unobtainable otherwise. Condensation of *p*-dimethylaminostyryl methyl ketone gave the desired ester and a high-melting

<sup>1</sup> E.g., Claisen, *Annalen*, 1896, **291**, 119.

<sup>2</sup> Schiff and Gigli, *Ber.*, 1898, **31**, 1306.

<sup>3</sup> Ruhemann, *J.*, 1909, **95**, 109.

<sup>4</sup> Ryan and Algar, *Proc. Roy. Irish Acad.*, 1913, **32**, 9.

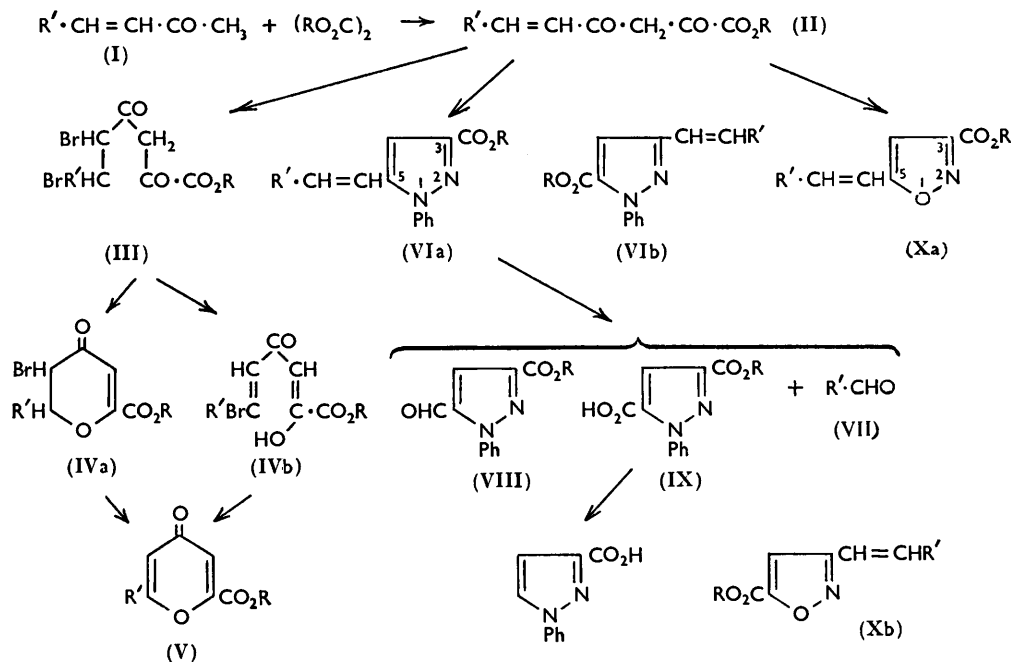
<sup>5</sup> Ryan and Plunkett, *ibid.*, 1916, **33**, 199.

product of undetermined structure; ethyl 6-*p*-dimethylaminophenyl-2:4-dioxohex-5-enoate readily loses its red colour in hydrochloric acid owing to engagement of the unshared electrons on the nitrogen by the hydrogen ion of the acid, resonance being thus prohibited.

We have utilised these esters in the synthesis of five new 6-aryl-4-pyrone-2-carboxylic esters (V), 1:3:5-trisubstituted pyrazoles (VI) and 3:5-disubstituted isooxazoles (Xa or b), likely to be of medicinal importance.

Attempts to obtain the dibromides of these esters by the methods described by Ryan and Algar<sup>4</sup> and by Borsche and Peter<sup>6</sup> for (III; R = Me, R' = *p*-MeO·C<sub>6</sub>H<sub>4</sub>) and (III; R = Et, R' = Ph), respectively, gave unsatisfactory results. However, they were prepared as described in the Experimental section and were converted into 6-aryl-4-pyrone-2-carboxylic esters by the action of potassium acetate in presence of calcium carbonate. In absence of the latter reagent, transesterification occurred in an alcohol different from that associated with the alkoxycarbonyl group of the dibromide used. There is no doubt about the constitution of these pyrones, since ethyl 6-phenyl-4-pyrone-2-carboxylate was converted into 2-phenyl-1:4-pyrone on acid hydrolysis and decarboxylation;<sup>6</sup> they were characterised as picrates and on fission gave the expected acidic and ketonic products.

Apparently, dehydrobromination with potassium acetate does not give an acetylenic 1:3-diketo-ester. Otherwise, the formation of these pyrones would proceed by addition of the enolate group to the acetylenic bond.<sup>7</sup> Instead, stepwise elimination of hydrogen bromide leads to either a bromodihydro-4-pyrone (IVa) before dehydrogenation, or a bromo-olefinic ester (IVb) before cyclisation. The second alternative has experimental support in the work of Wislicenus<sup>8</sup> and Abell<sup>9</sup> who obtained  $\omega$ -benzylidene- $\omega$ -bromoacetophenone by the action of potassium acetate on benzylideneacetophenone dibromide.



With phenylhydrazine the unsaturated 1:3-diketo-esters (II) gave the pyrazoles (VIa) and, again, transesterification was inevitable in acidic media. That these trisubstituted pyrazoles were obtained pure from the reaction medium is evidence that only one carbonyl

<sup>6</sup> Borsche and Peter, *Annalen*, 1927, **453**, 148.

<sup>7</sup> Soliman and El-Kholy, *J.*, 1954, 1755.

<sup>8</sup> Wislicenus, *Annalen*, 1899, **308**, 219.

<sup>9</sup> Abell, *J.*, 1912, **101**, 998.

group is involved in the primary condensation, which gave the ester (VIa) and not (VIb) since ozonolysis gave the aromatic aldehydes (VII), the aldehydic ester (VIII), and the monoester of 1-phenylpyrazole-3 : 5-dicarboxylic acid (IX), whose identity was established by hydrolysis to the free dicarboxylic acid.<sup>10, 11</sup> The 5 position assigned to the free carboxylic group is confirmed by ready decarboxylation of the half-ester (IX) to a neutral ester which was hydrolysed to 1-phenylpyrazole-3-carboxylic acid.<sup>10</sup>

Analogously, the 3 : 5-disubstituted isooxazoles which have been prepared may be assigned the formula (Xa) [rather than (Xb)] in agreement with Musante's<sup>12</sup> suggestion for ethyl 5-styrylisooxazole-3-carboxylate.

#### EXPERIMENTAL

Light petroleum used had b. p. 60—80°.

*Ethyl 2 : 4-Dioxo-6-phenylhex-5-enoate*.—Methyl styryl ketone (10 g., 1 mol.) and ethyl oxalate (10 g., 1 mol.) were added to an ice-cold suspension of sodium ethoxide (4.4 g., 1 mol.) in dry ether (100 ml.). The mixture was kept overnight at room temperature and the sodium salt was separated and acidified with 10% sulphuric acid. The recovered ester (14.8 g.) crystallised from ethanol in yellow needles, m. p. 84°, which gave a red colour with ferric chloride.

Methyl 2 : 4-dioxo-6-phenylhex-5-enoate was obtained when the ethyl ester (1 g.) was refluxed in methanol (5 ml.) containing one drop of concentrated sulphuric acid for 1 hr. It crystallised from methanol in yellow needles, m. p. 70°.

Both esters gave with 5% aqueous titanium trichloride<sup>13</sup> a blackish-brown colour which changed into bluish  $\rightarrow$  violet  $\rightarrow$  colourless.

*Ethyl 5 : 6-Dibromo-2 : 4-dioxo-6-phenylhexanoate*.—This was obtained quantitatively when an ice-cold 10% solution (65 ml.) of bromine in carbon disulphide was added to ethyl 2 : 4-dioxo-6-phenylhex-5-enoate (10 g.) in cold carbon disulphide (50 ml.). The mixture was kept cool overnight; the dibromide recovered by evaporation of the solvent at room temperature crystallised from ethanol in pale yellow needles, m. p. 107°.<sup>6</sup>

*Ethyl 6-Phenyl-4-pyrone-2-carboxylate*.—The foregoing dibromide (5 g.), fused potassium acetate (5 g.), calcium carbonate (5 g.), and absolute ethanol (30 ml.) were heated at 60—70° for 3 hr. The pyrone (1.8 g.) was recovered after concentration of the alcoholic solution, dilution with water, and extraction with ether. It crystallised from water in needles, m. p. 119° (Found : C, 68.6; H, 5.2. Calc. for C<sub>14</sub>H<sub>12</sub>O<sub>4</sub> : C, 68.9; H, 5.0%). The *picrate* was prepared in alcohol and crystallised from alcohol in yellow needles, m. p. 130° (Found : N, 8.9. C<sub>20</sub>H<sub>15</sub>O<sub>11</sub>N<sub>3</sub> requires N, 8.9%).

*Methyl 6-phenyl-4-pyrone-2-carboxylate* was obtained when ethyl 5 : 6-dibromo-2 : 4-dioxo-6-phenylhexanoate (3 g.) was heated with fused potassium acetate (3 g.) in absolute methanol (25 ml.) for 5 hr. The pyrone was recovered as above and crystallised from boiling water in plates, m. p. 127° (Found : C, 68.1; H, 4.2; OMe, 13.4. C<sub>13</sub>H<sub>10</sub>O<sub>4</sub> requires C, 67.8; H, 4.4; OMe, 13.5%). The two esters yielded 6-phenyl-4-pyrone-2-carboxylic acid,<sup>6</sup> m. p. 233°, when boiled with concentrated hydrochloric acid; this crystallised from water in needles, m. p. 238°.

*Fission of the Pyrone*.—Ethyl 6-phenyl-4-pyrone-2-carboxylate (0.5 g.) was refluxed with 20% aqueous potassium hydroxide (10 ml.) in an all-glass apparatus for 20 min. The mixture was then steam-distilled and the first 10 ml. of the ketonic distillate were collected separately. Subsequently, the alkaline mixture was acidified with 10% hydrochloric acid and steam-distilled. The first ketonic distillate gave a positive test for acetone, and the main ketonic distillate contained acetophenone.<sup>7</sup> The acidic distillate yielded 0.2 g. of benzoic acid and gave a positive test for acetic acid. The non-volatile residue was neutralised with aqueous ammonia and mixed with calcium chloride solution, and the precipitate obtained was identified as calcium oxalate by the aniline-blue test.<sup>14</sup>

*Ethyl 1-Phenyl-5-styrylpyrazole-3-carboxylate*.—This was prepared when a solution of the above ethyl hexenoate (2 g.) in ethanol (10 ml.) was refluxed with phenylhydrazine hydrochloride (1 g.) and sodium acetate (0.8 g.) in water (3 ml.) for 1 hr. It crystallised from ethanol in needles, m. p. 120°.

<sup>10</sup> Claisen, *Ber.*, 1891, **24**, 1888.

<sup>11</sup> Keskin, *Rev. Fac. Sci. Univ. Istanbul*, 1944, **9**, A, 81.

<sup>12</sup> Musante, *Gazzetta*, 1942, **72**, 134.

<sup>13</sup> Weygand and Csendes, *Chem. Ber.*, 1952, **85**, 45.

<sup>14</sup> Vogel, "Qualitative Chemical Analysis," Longmans, Green and Co., 1951, p. 311.

A chloroform solution of the ester (2 g.) was treated with ozonised oxygen, and after removal of the solvent, the ozonide was decomposed and distilled with steam until benzaldehyde ceased to pass over. The non-volatile residue was extracted with ether, and the ethereal solution shaken with sodium hydrogen carbonate solution. *Ethyl 5-formyl-1-phenylpyrazole-3-carboxylate* (VIII) (0.8 g.) was recovered from the neutral ethereal solution and crystallised from light petroleum in needles, m. p. 89° (Found : C, 63.9; H, 4.8; N, 11.4.  $C_{13}H_{12}O_3N_2$  requires C, 63.9; H, 4.95; N, 11.5%). Its *oxime* crystallised from benzene-light petroleum in needles, m. p. 154° (Found : C, 60.2; H, 5.2; N, 16.2.  $C_{13}H_{13}O_3N_3$  requires C, 60.2; H, 5.05; N, 16.2%).

*3-Ethoxycarbonyl-1-phenylpyrazole-5-carboxylic acid* (IX) (0.6 g.) was recovered from the sodium hydrogen carbonate extract and crystallised from benzene in needles, m. p. 164° (Found : C, 59.6; H, 4.9; N, 10.4.  $C_{13}H_{12}O_4N_2$  requires C, 60.0; H, 4.65; N, 10.8%). It was also obtained by oxidation of the above aldehyde (VIII) with powdered potassium permanganate in acetone.

*1-Phenylpyrazole-3 : 5-dicarboxylic Acid*.—This acid<sup>11</sup> was obtained by hydrolysis of the foregoing monoester (0.1 g.) in boiling dilute hydrochloric acid (1 : 1) (4 ml.) for 1 hr., and crystallised from water in needles, m. p. 266°.

*1-Phenylpyrazole-3-carboxylic Acid*.—*3-Ethoxycarbonyl-1-phenylpyrazole-5-carboxylic acid* (0.4 g.) was decarboxylated at 180—185°. The oily residue was shaken in ether with sodium hydrogen carbonate solution. The ester recovered from the ethereal solution was hydrolysed by boiling with hydrochloric acid (1 : 1) (10 ml.) for 1 hr. The acid, m. p. 137°, which separated on cooling, crystallised from water in needles, m. p. 143° (Found : C, 63.5; H, 4.1. Calc. for  $C_{10}H_8O_2N_2$  : C, 63.8; H, 4.3%). Its methyl ester, prepared by diazomethane, crystallised from light petroleum in prisms, m. p. 72° (Found : C, 65.2; H, 5.0. Calc. for  $C_{11}H_{10}O_2N_2$  : C, 65.3; H, 5.0%).

*Ethyl 5-Styrylisooxazole-3-carboxylate*.—This was prepared when the above ethyl hexenoate (2 g.) in ethanol (20 ml.) was refluxed with hydroxylamine hydrochloride (0.7 g.) and sodium acetate (0.8 g.) in water (3 ml.) for 2 hr. It crystallised from ethanol in needles, m. p. 112°. The methyl ester, m. p. 143°, was obtained in a methanolic medium in absence of sodium acetate.

*Ethyl 6-p-Methoxyphenyl-2 : 4-dioxohex-5-enoate*.—This ester was prepared in 90% yield from 4-methoxystyryl methyl ketone and crystallised from ethanol in yellow needles, m. p. 92° (Found : C, 65.2; H, 5.9.  $C_{15}H_{16}O_5$  requires C, 65.2; H, 5.8%). It gave a reddish-brown colour with ferric chloride and a reddish-brown colour which changed to brown → bluish → colourless with titanium trichloride. It gave on methanolysis the methyl ester which crystallised from methanol in yellow needles, m. p. 128°.

*Methyl 5 : 6-Dibromo-6-p-methoxyphenyl-2 : 4-dioxohexanoate*.—The dibromide was prepared in 87% yield from the above methyl ester and crystallised from carbon tetrachloride in pale yellow needles, m. p. 118° (Found : C, 39.4; H, 3.2; Br, 37.8. Calc. for  $C_{14}H_{14}O_5Br_2$  : C, 39.8; H, 3.3; Br, 37.9%).

*Methyl 6-p-Methoxyphenyl-4-pyrone-2-carboxylate*.—This pyrone was prepared in 70% yield by heating the foregoing dibromide with potassium acetate and calcium carbonate in methanol for 4 hr. It crystallised from water in needles, m. p. 131—133° (Found : C, 64.5; H, 4.5.  $C_{14}H_{12}O_5$  requires C, 64.6; H, 4.65%). Its *picrate* crystallised from ethanol in yellow needles, m. p. 110° (Found : N, 8.7.  $C_{20}H_{15}O_{12}N_3$  requires N, 8.6%). The pyrone was degraded with 20% aqueous potassium hydroxide to acetone, 4-methoxyacetophenone, and *p*-anisic, oxalic, and acetic acid.

*Ethyl 5-4'-Methoxystyryl-1-phenylpyrazole-3-carboxylate*.—This ester crystallised from ethanol in needles, m. p. 100° (Found : C, 72.4; H, 5.8; N, 8.15.  $C_{21}H_{20}O_3N_2$  requires C, 72.4; H, 5.8; N, 8.0%). Its *picrate* crystallised from ethanol in yellow needles, m. p. 88° (Found : N, 12.0.  $C_{27}H_{22}O_{10}N_5$  requires N, 12.1%). It yielded on ozonolysis *p*-anisaldehyde, the pyrazole aldehyde (VIII), and the mono-ester (IX).

Methods analogous to those above gave the following compounds :

*Ethyl 5-4'-methoxystyryl-isooxazole-3-carboxylate*, needles (from ethanol), m. p. 77°. The *methyl* analogue crystallised from methanol in plates, m. p. 137° (Found : C, 65.1; H, 4.9; N, 5.7.  $C_{14}H_{13}O_4N$  requires C, 64.8; H, 5.05; N, 5.4%).

*Ethyl 6-o-methoxyphenyl-2 : 4-dioxo-5-hexenoate* (90% from 2-methoxystyryl methyl ketone<sup>15</sup>), orange needles (from methanol), m. p. 80° (Found : C, 65.0; H, 5.9; OEt, 15.9.  $C_{15}H_{16}O_5$

<sup>15</sup> Shoemith and Connor, *J.*, 1927, 2231.

requires C, 65.2; H, 5.8; OEt, 16.3%); it gave a reddish-brown colour with ferric chloride, and a reddish-brown colour which changed into brown  $\rightarrow$  bluish  $\rightarrow$  colourless with titanium trichloride. The *methyl ester*, prepared by methanolysis, crystallised from methanol in orange needles, m. p. 97° (Found: C, 64.0; H, 5.3; OMe, 24.0.  $C_{14}H_{14}O_5$  requires C, 64.1; H, 5.4; 2OMe, 23.7%).

*Methyl 5 : 6-dibromo-6-o-methoxyphenyl-2 : 4-dioxohexanoate* (84%), yellowish-white plates (from carbon tetrachloride), m. p. 133° (Found: C, 39.4; H, 3.3; Br, 38.0.  $C_{14}H_{14}O_5Br_2$  requires C, 39.8; H, 3.3; Br, 37.9%).

*Methyl 6-o-methoxyphenyl-4-pyrone-2-carboxylate* (81%), needles (from water), m. p. 148° (Found: C, 64.5; H, 4.5.  $C_{14}H_{12}O_5$  requires C, 64.6; H, 4.65%).

*Ethyl 5-2'-methoxystyryl-1-phenylpyrazole-3-carboxylate*, prisms (from methanol), m. p. 80° (Found: C, 72.6; H, 5.6; N, 8.2.  $C_{21}H_{20}O_3N_2$  requires C, 72.4; H, 5.8; N, 8.0%); *picrate*, yellow needles (from methanol), m. p. 85° (Found: N, 12.1.  $C_{27}H_{23}O_{10}N_5$  requires N, 12.1%). It gave on ozonolysis *o*-anisaldehyde, the aldehyde (VIII), and the mono-ester (IX).

*Ethyl 5-2'-methoxystyrylisooxazole-3-carboxylate* (recovered from the reaction mixture by dilution and extraction with ether), prisms (from light petroleum), m. p. 56° (Found: C, 65.8; H, 5.4; N, 5.05.  $C_{15}H_{15}O_4N$  requires C, 65.9; H, 5.5; N, 5.1%).

*Ethyl 6-(3 : 4-dimethoxyphenyl)-2 : 4-dioxohex-5-enoate* (98%), orange needles (from ethanol), m. p. 99° (Found: C, 62.4; H, 5.9; OEt, 14.1.  $C_{16}H_{16}O_6$  requires C, 62.7; H, 5.9; OEt, 14.7%). It gave a brown colour with ferric chloride, a violet colour with sulphuric acid, and a reddish-brown colour which changed into brown  $\rightarrow$  colourless with titanium trichloride.

*Ethyl 5 : 6-dibromo-6-(3 : 4-dimethoxyphenyl)-2 : 4-dioxohexanoate*, prisms, m. p. 134° (from carbon tetrachloride) (Found: Br, 35.3.  $C_{16}H_{16}O_6Br_2$  requires Br, 34.3%), was dehydrobrominated to *ethyl 6-(3 : 4-dimethoxyphenyl)-4-pyrone-2-carboxylate* in absolute ethanol (yield, 72%), prisms (from ethanol), m. p. 175° (Found: C, 63.0; H, 5.3.  $C_{16}H_{16}O_6$  requires C, 63.1; H, 5.3%).

*Ethyl 5-(3 : 4-dimethoxystyryl)-1-phenylpyrazole-3-carboxylate*, long needles (from ethanol), m. p. 113° (Found: C, 69.7; H, 5.9; N, 7.4.  $C_{22}H_{22}O_4N_2$  requires C, 69.81; H, 5.9; N, 7.4%). It gave on ozonolysis the mono-ester (IX).

*Ethyl 6-(3 : 4-methylenedioxyphenyl)-2 : 4-dioxohex-5-enoate*, orange prisms (from acetone), m. p. 130° (Found: C, 62.05; H, 4.9; OEt, 15.8.  $C_{15}H_{14}O_6$  requires C, 62.05; H, 4.9; OEt, 15.5%). It gave a brown colour with ferric chloride, a violet colour with sulphuric acid, and a reddish-brown colour which changed into brown  $\rightarrow$  colourless with titanium trichloride.

*Ethyl 5 : 6-dibromo-6-(3 : 4-methylenedioxyphenyl)-2 : 4-dioxohexanoate*, prisms (from carbon tetrachloride), m. p. 117° (Found: C, 40.0; H, 3.05; Br, 35.6.  $C_{15}H_{14}O_6Br_2$  requires C, 40.0; H, 3.1; Br, 35.5%).

*Ethyl 6-(3 : 4-methylenedioxyphenyl)-4-pyrone-2-carboxylate* (81%), yellowish-white needles (from benzene-light petroleum), m. p. 161° (Found: C, 62.2; H, 4.1.  $C_{15}H_{12}O_6$  requires C, 62.5; H, 4.2%).

*Ethyl 5-(3 : 4-methylenedioxyphenyl)-1-phenylpyrazole-3-carboxylate*, long needles (from ethanol), m. p. 191° (Found: C, 69.2; H, 4.9; N, 7.8.  $C_{21}H_{18}O_4N_2$  requires C, 69.6; H, 5.0; N, 7.7%).

*Ethyl 5-(3 : 4-methylenedioxyphenyl)isooxazole-3-carboxylate*, needles (from ethanol), m. p. 122° (Found: C, 63.0; H, 4.7; N, 5.2.  $C_{15}H_{13}O_5N$  requires C, 62.7; H, 4.6; N, 4.9%).

*Ethyl 6-2'-furyl-2 : 4-dioxohex-5-enoate*, yellow needles [from light petroleum (b. p. 60–80°)], m. p. 80° (Found: C, 60.8; H, 5.0; OEt, 18.9.  $C_{12}H_{12}O_5$  requires C, 61.0; H, 5.1; OEt, 19.1%). The *methyl ester*, obtained by methanolysis, crystallised from methanol in needles, m. p. 100° (Found: C, 59.7; H, 4.6; OMe, 13.6.  $C_{11}H_{10}O_5$  requires C, 59.5; H, 4.5; OMe, 14.0%). Both esters gave a dark-brown colour with ferric chloride, a dark red colour with sulphuric acid, and a reddish-brown colour which changed into bluish  $\rightarrow$  violet  $\rightarrow$  colourless with titanium trichloride.

*Ethyl 6-2'-furyl-4-pyrone-2-carboxylate*.—The purified dibromide (5 g.), m. p. 101°, prepared from the foregoing ester was dehydrobrominated for 2 hr. The ethanolic filtrate was concentrated, diluted with water, and extracted with ether, and the residue (2.6 g.) recovered was extracted with light petroleum. The latter extract yielded the *pyrone* (1 g.) which crystallised from light petroleum in needles, m. p. 103° (Found: C, 60.9; H, 4.4.  $C_{12}H_{10}O_5$  requires C, 61.5; H, 4.3%).

*Ethyl 5-(2-2'-furylvinyl)pyrazole-3-carboxylate* crystallised from ethanol in needles, m. p. 116° (Found: C, 70.5; H, 5.3; N, 9.2.  $C_{18}H_{16}O_3N_2$  requires C, 70.1; H, 5.3; N, 9.1%).

*Ethyl 5-(2-2'-furylvinyl)isooxazole-3-carboxylate* crystallised from ethanol in needles, m. p. 104° (Found: C, 61.8; H, 4.7; N, 6.3.  $C_{12}H_{11}O_4N$  requires 61.8; H, 4.8; N, 6.0%).

*Ethyl 6-p-Dimethylaminophenyl-2 : 4-dioxohex-5-enoate*.—This was prepared by condensation of *p*-dimethylaminostyryl methyl ketone <sup>16</sup> (10 g., 1 mol.) with ethyl oxalate (8.1 g., 1 mol.). The sodium salt was acidified with acetic acid, a deep-red solid (15 g.), m. p. 115°, separating. When refluxed with light petroleum, the ester was extracted, leaving an insoluble brown dye (5 g.), m. p. 190°. The *ester* crystallised from light petroleum in red plates, m. p. 122° (Found : C, 66.5; H, 6.6; N, 4.6. C<sub>16</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 66.4; H, 6.6; N, 4.8%). It gave a reddish-brown colour with ferric chloride, and a deep-red colour which changed into brown → black → colourless with titanium trichloride. Its solution in hydrochloric acid is only pale-yellow. The dye crystallised from benzene in brown aggregate needles, m. p. 190° (Found : C, 71.9; H, 7.4; N, 8.5%).

*Ethyl 5-p-dimethylaminostyryl-1-phenylpyrazole-3-carboxylate* crystallised from ethanol in prisms, m. p. 114° (Found : C, 72.6; H, 6.4; N, 11.6. C<sub>22</sub>H<sub>23</sub>O<sub>2</sub>N<sub>3</sub> requires C, 73.1; H, 6.4; N, 11.6%). It gave on ozonolysis the monoester (IX).

*Ethyl 5-p-dimethylaminostyrylisooxazole-3-carboxylate* crystallised from ethanol in prisms, m. p. 123° (Found : C, 66.8; H, 6.3; N, 10.0. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub> requires C, 67.1; H, 6.3; N, 9.8%).

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<sup>16</sup> Sachs and Lewin, *Ber.*, 1902, **35**, 3569.

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