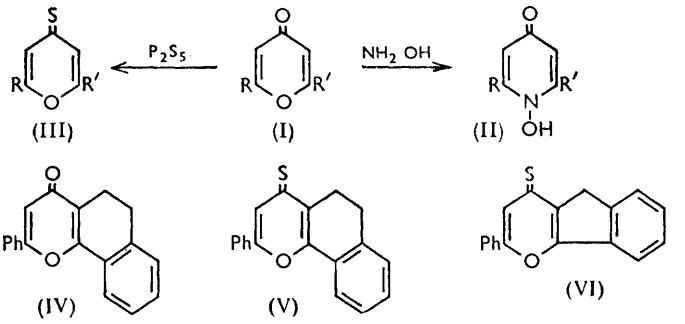
516. *Pyrone Series. Part III.*[1] 2,6-*Diaryl*-4-*thiopyrones and* -5-*methoxy*-2-*pyrones and Thio-analogues of the Latter.*

By Ibrahim El-Sayed El-Kholy, Fathi Kamel Rafla, and Gabra Soliman.

Several 2,6-diaryl-4-thiopyrones have been prepared and converted into the corresponding 4-hydroxyimino-derivatives. 4,6-Diaryl-5-methoxy-2-pyrones have been synthesised by condensation of ω-methoxyacetophenones with ethyl arylpropiolates. The structures of the latter pyrones have been determined by alkaline fission, and they have been converted into 2-thiopyrones, 2-pyridones, and 1-amino-2-pyridones.

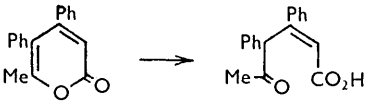
In continuation of our synthesis of 2,6-diaryl-4-pyrones[2] (I), 2,6-di-*p*-methoxyphenyl-4-pyrone and 5,6-dihydro-7,8-benzoflavone (IV) have been prepared by condensation of ethyl *p*-methoxyphenylpropiolate with *p*-methoxyacetophenone and of ethyl phenylpropiolate with 1-tetralone, respectively.

Alkaline degradation of 2,6-di-*p*-methoxyphenyl-4-pyrone gave acetone, *p*-methoxyacetophenone, and *p*-anisic acid in agreement with the structure suggested. There is some doubt, however, regarding the structure of 5,6-dihydro-7,8-benzoflavone which appears to be the outcome of Claisen condensation, a reaction already known for 1-tetralone;[3] investigation of the structure of this pyrone involving dehydrogenation and degradation is in progress.



These two pyrones (I; R = R′ = C_6H_4·OMe-*p*) and (IV), as well as 6-phenylindeno-(3′,2′-2,3)pyrone[2] gave stable picrates, but failed to react with hydroxylamine. Earlier,[2] 1-hydroxypyridones (II) were obtained by the action of hydroxylamine on 2,6-diaryl-4-pyrones (I). In the present study, the pyrone oximes have been prepared by the action of hydroxylamine on the 4-thio-derivatives (III, V, and VI). 2-Methyl-6-phenyl-4-thiopyrone failed to give an oxime.

Traverso[4] obtained 3,4-diphenylbut-2-enoic acid on hydrolysis of 4,5,6-triphenyl- or 6-methyl-4,5-diphenyl-2-pyrone. In our hands, the latter pyrone was hydrolysed to *cis*-5-oxo-3,4-diphenylhex-2- or -3-enoic acid, the methyl ester of which was cyclised to



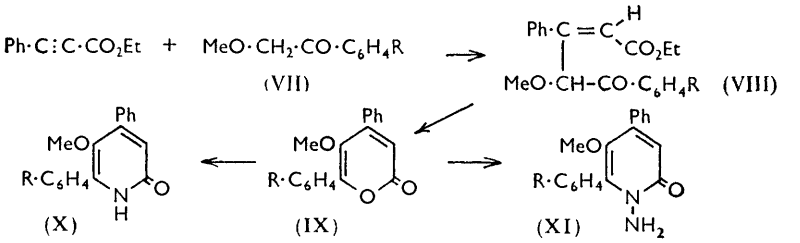
the pyrone. Contrary to Traverso's report,[4] 6-benzyl-4,5-diphenyl-2-pyrone underwent ring fission, but the free acid readily cyclised. Attempted methylation in an alkaline medium led to two neutral compounds which are being studied.

[1] Part II, *J.*, 1955, 2911.
[2] Soliman and El-Kholy, *J.*, 1954, 1755.
[3] Hückel and Goth, *Ber.*, 1924, **57**, 1288.
[4] Traverso, *Boll. sci. Fac. Chim. ind. Bologna*, 1955, **13**, 53.

4,6-Diaryl-5-methoxy-2-pyrones (IX) have now been prepared by condensation of ethyl phenylpropiolate with ω-methoxyacetophenones (VII; R = H, Me, or OMe), and 5-methoxy-4,6-di-*p*-methoxyphenyl-2-pyrone has been obtained from ethyl *p*-methoxyphenylpropiolate and ω-4-dimethoxyacetophenone (VII; R = OMe). However, none of these pyrones was accompanied by an intermediate Michael addition product which can be looked upon as the *trans*-isomer of the hypothetical *cis*-3,5-diaryl-4-methoxy-5-oxopent-2-enoic ester (VIII). Moreover, alkaline fission of these pyrones gave products, presumably *cis*-3,5-diaryl-4-methoxy-5-oxopent-2- or -3-enoic acids, whose methyl esters cyclised to the pyrones.

In addition to 4,6-diphenyl-2-thiopyrone synthesised by Arndt and Eistert,[5] we have prepared 5-methoxy-4,6-diphenyl-, 5-methoxy-4-phenyl-6-*p*-tolyl-, 5-methoxy-6-*p*-methoxyphenyl-4-phenyl-2-thiopyrones and 5-methoxy-4,6-di-*p*-methoxyphenyl-2-thiopyrone by the action of phosphorus pentasulphide on the corresponding pyrones. Unlike 2,6-diaryl-4-thiopyrones, these 2-thiopyrones are readily hydrolysed to the original 2-pyrones (IX) by hydroxylamine or hydrazine hydrate, but not by semicarbazide. An additional difference between 2,6-diaryl-4-pyrones and 5-methoxy-4,6-diaryl-2-pyrones is that the latter do not give 1-hydroxy-2-pyridones: 5-methoxy-4,6-diphenyl-2-pyrone is the only exception since it reacted with hydroxylamine with difficulty, giving the 1-hydroxy-2-pyridone.

Although the formation of 4-pyridones and 2-pyridones (X) from 2,6-diaryl-4-pyrones (I) and 5-methoxy-4,6-diaryl-2-pyrones (IX) is equally possible by ammonolysis, yet they differ in some of their properties. The 4-pyridones are susceptible to acid-catalysed hydrolysis to pyrones,[6] whereas the 2-pyridones are stable, tending to exist in the enolic form.[7] Hauser and Eby [8] recently obtained a similar series of polysubstituted 2-pyridones by cyclisation of β-keto-nitriles or β-keto-amides with ketones by polyphosphoric acid.



Further, by the action of hydrazine hydrate on 4,6-diaryl-5-methoxy-2-pyrones, we have prepared a series of 1-amino-2-pyridones (XI). These gave the characteristic reactions of the 1-amino-2-pyridones recently synthesised by condensation of chloramine with 2-pyridones.[9] On the other hand, α-(3-phenyl-5-pyrazolyl)acetophenone hydrazone has been prepared by the action of hydrazine hydrate on 2,6-diphenyl-4-pyrone, presumably through a triketone;[10] having *sym*-dibenzoylacetone available, we have confirmed this mechanism by preparing from it the pyrazole in question (cf. 5-β-hydroxyiminophenethyl-3-phenylisoxazole [1]).

Experimental

Light petroleum used had b. p. 50—70°.

2,6-*Di*-p-*methoxyphenyl*-4-*pyrone*.—Ethyl *p*-methoxyphenylpropiolate [11] was prepared by saturation of an ice-cold solution of *p*-methoxyphenylpropiolic acid [12] (20·1 g.) in absolute

[5] Arndt and Eistert, *Ber.*, 1925, **58**, 2318.
[6] Neelakantan, *J. Org. Chem.*, 1958, **23**, 741.
[7] Elderfield, "Heterocyclic Compounds," John Wiley and Sons, New York, 1950, Vol. I, p. 439.
[8] Hauser and Eby, *J. Amer. Chem. Soc.*, 1957, **79**, 728.
[9] Hoegerle, *Helv. Chim. Acta*, 1958, **41**, 539.
[10] Ainsworth and Jones, *J. Amer. Chem. Soc.*, 1954, **76**, 3172.
[11] Hariharan and Sudborough, *J. Indian. Inst. Sci.*, 1925, **8**, *A*, 193.
[12] Baddar and L. S. El-Assal, *J.*, 1948, 1269.

ethanol (120 ml.) with hydrogen chloride. After being kept for 6 hr. at room temperature, the mixture was poured into ice-cold water, and the ester (20·0 g.), recovered by extraction with ether, was purified by distillation at 158—160°/3 mm.

p-Methoxyacetophenone (2·6 g., 1 mol.) and *p*-methoxyphenylpropiolate (3·5 g., 1 mol.) were added to sodium ethoxide (1·45 g., 1·25 mol.) in dry ether (150 ml.), and the mixture kept at 0° for 36 hr. The brown oil (4·0 g.) recovered from the neutral ethereal solution yielded the pyrone (0·3 g.), m. p. 183°, on treatment with light petroleum. It crystallised from benzene–light petroleum in yellowish needles, m. p. 192°. The alkaline solution yielded 1·2 g. of *p*-methoxyphenylpropiolic acid and a non-acidic oil which afforded an additional 0·2 g. of the pyrone.

2,6-*Di*-p-*methoxyphenyl*-4-*pyrone picrate* was prepared in benzene and crystallised from acetone in needles, m. p. 221° (Found: C, 55·9; H, 3·5; N, 8·0; OMe, 11·4. $C_{25}H_{19}O_{11}N_3$ requires C, 55·9; H, 3·6; N, 7·8; OMe, 11·55%).

The colourless pyrone was recovered by decomposition of the picrate with aqueous ammonia and crystallised from methanol in needles, m. p. 195° (lit.,[13] m. p. 189—190°) (Found: C, 73·75; H, 5·3; OMe, 20·1. Calc. for $C_{19}H_{16}O_4$: C, 74·0; H, 5·2; OMe, 20·1%). It was recovered unchanged after being heated with hydroxylamine for 9 hr.

About 50% of 2,6-di-*p*-methoxyphenyl-4-pyrone was degraded by boiling 40% aqueous potassium hydroxide in 6 hr. as previously described.[2] It yielded *p*-anisic acid, m. p. 184°, acetone, and *p*-methoxyacetophenone (2 : 4-dinitrophenylhydrazone, m. p. 207—208°).

5,6-*Dihydro*-7,8-*benzoflavone* (IV).—This was prepared by condensation of 1-tetralone[14] (4·2 g.) with ethyl phenylpropiolate (5·0 g.) as usual.[2] After 4 days in the ice-chest, the green mixture lost its viscosity and became dark brown. The reddish oily residue (6·4 g.) recovered from the neutral ethereal solution deposited the pyrone (0·5 g.), m. p. 150°, at room temperature. It crystallised from benzene–light petroleum in yellowish needles, m. p. 174°. Phenylpropiolic acid (2 g.) was recovered from the alkaline solution. Its *picrate* crystallised from benzene in plates, m. p. 196° (Found: N, 8·5. $C_{25}H_{17}O_9N_3$ requires N, 8·35%). Decomposition with aqueous ammonia yielded the *pyrone*, needles (from benzene–light petroleum), m. p. 174° (Found: C, 83·3; H, 5·0. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·15%). The pyrone was recovered unchanged after being heated with hydroxylamine for 20 hr.

2,6-*Di*-p-*methoxyphenyl*-4-*thiopyrone*.—This was prepared when a solution of 2,6-di-*p*-methoxyphenyl-4-pyrone (0·5 g.) in benzene was boiled with phosphorus pentasulphide (1·0 g.) for 1 hr. The orange-red solution was separated, washed with ammonium sulphide, then with water, dried, and distilled. The residue (0·5 g.) yielded the crude thiopyrone, m. p. 160°, on treatment with light petroleum. It crystallised from benzene–light petroleum in brown needles, m. p. 185° (lit.,[13] m. p. 180°) (Found: C, 70·6; H, 5·2; S, 9·7. Calc. for $C_{19}H_{16}O_3S$: C, 70·4; H, 5·0; S, 9·9%).

2,6-*Di*-p-*methoxyphenyl*-4-*pyrone oxime* was obtained when a solution of the thiopyrone (0·3 g.) in ethanol (70 ml.) was refluxed with a solution of hydroxylamine hydrochloride (0·4 g.) and sodium acetate (0·4 g.) in water (2 ml.) for 5 hr. When the mixture was diluted with a few drops of water, the unchanged thiopyrone (0·1 g.) was recovered. On further dilution of the filtrate, the oxime (0·2 g.), m. p. 173°, separated. It crystallised from benzene–light petroleum in yellow needles, m. p. 182° (Found: C, 71·0; H, 5·5; N, 4·3. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3; N, 4·3%).

5,6-*Dihydro*-4-*thio*-7,8-*benzoflavone*.—This *compound* was prepared from the dihydroflavone (IV) as above and crystallised from benzene–light petroleum in red prisms, m. p. 183° (Found: C, 78·7; H, 4·9; S, 10·95. $C_{19}H_{14}OS$ requires C, 78·6; H, 4·9; S, 11·0%).

An ethanolic solution of the thiopyrone (0·7 g.) was refluxed with hydroxylamine hydrochloride (0·7 g.) and sodium acetate (0·7 g.) in water (2 ml.) for 7 hr. After dilution and cooling, a mixture (0·7 g.), m. p. 174°, of the oxime and the thiopyrone separated. It was treated with benzene and the insoluble *oxime* (0·3 g.), m. p. 232° (decomp.), crystallised from pyridine–ethanol in yellow needles, m. p. 240° (decomp.) (Found: C, 79·0; H, 5·3; N, 4·8. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 4·8%).

The following 4-thiopyrones were prepared from known pyrones;[2] therefrom oximes (yellow needles) were prepared by means of hydroxylamine in hot ethanol (3 hr.) and isolated either by dilution or by dilution and extraction with ether.

[13] Schönberg, Elkaschef, Nosseir, and Sidky, *J. Amer. Chem. Soc.*, 1958, **80**, 6314.
[14] *Org. Synth.*, 1940, **20**, 94; Brown, Widiger, and Letang, *J. Amer. Chem. Soc.*, 1939, **61**, 2601.

2-*Phenyl*-6-p-*tolyl*-4-*thiopyrone*, pale brown needles, m. p. 142° (from methanol) (Found: C, 77·6; H, 5·0; S, 11·5. $C_{18}H_{14}OS$ requires C, 77·7; H, 5·1; S, 11·5%).

2-p-*Methoxyphenyl*-6-*phenyl*-4-*thiopyrone*, brown needles, m. p. 185—186° (from benzene–light petroleum) (Found: C, 73·7; H, 4·8; S, 11·0; OMe, 10·4. $C_{18}H_{14}O_2S$ requires C, 73·5; H, 4·8; S, 10·9; OMe, 10·5%).

2-p-*Chlorophenyl*-6-*phenyl*-4-*thiopyrone*, brown needles, m. p. 156° (from ethanol) (Found: C, 68·35; H, 3·8; Cl, 12·3; S, 10·3. $C_{17}H_{11}OClS$ requires C, 68·3; H, 3·7; Cl, 11·9; S, 10·7%).

2-p-*Bromophenyl*-6-*phenyl*-4-*thiopyrone*, needles, m. p. 170—172° (from carbon tetrachloride) (Found: C, 59·2; H, 3·1; S, 9·8. $C_{17}H_{11}OBrS$ requires C, 59·5; H, 3·2; S, 9·3%).

6-*Phenyl*-4-*thioindeno*(3′,2′-2,3)*pyrone* (VI), orange needles, m. p. 186° (from benzene–light petroleum) (Found: C, 78·1; H, 4·6; S, 11·4. $C_{18}H_{12}OS$ requires C, 78·25; H, 4·4; S, 11·6%).

2-*Methyl*-6-*phenyl*-4-*thiopyrone* (prepared from the pyrone [15]), brown needles (from benzene–light petroleum), m. p. 117° [16] (Found: C, 71·4; H, 5·05; S, 15·1. Calc. for $C_{12}H_{10}OS$: C, 71·2; H, 5·0; S, 15·85%).

2-*Phenyl*-6-p-*tolyl*-4-*pyrone oxime*, m. p. 194° (decomp.) (from benzene–ethanol) (Found: C, 77·9; H, 5·4; N, 5·2. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·45; N, 5·05%).

2-p-*Methoxyphenyl*-6-*phenyl*-4-*pyrone oxime*, m. p. 194° (decomp.) (from ethanol) (Found: C, 73·5; H, 5·2; N, 4·7; OMe, 10·4. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·2; N, 4·8; OMe, 10·6%).

2-p-*Chlorophenyl*-6-*phenyl*-4-*pyrone oxime*, m. p. 226° (decomp.) (from pyridine–ethanol) (Found: C, 68·6; H, 4·2; N, 4·6. $C_{17}H_{12}O_2NCl$ requires C, 68·5; H, 4·1; N, 4·7%).

2-p-*Bromophenyl*-6-*phenyl*-4-*pyrone oxime*, m. p. 230° (decomp.) (from pyridine–ethanol) (Found: C, 59·85; H, 3·5; N, 3·9; Br, 23·1. $C_{17}H_{12}O_2NBr$ requires C, 59·6; H, 3·5; N, 4·1; Br, 23·35%).

6-*Phenylindeno*(3′,2′-2,3)*pyrone oxime*, m. p. 252° (decomp.) (from pyridine–ethanol) (Found: C, 78·9; H, 4·7; N, 5·0. $C_{18}H_{13}O_2N$ requires C, 78·5; H, 4·8; N, 5·1%).

6-Phenylindeno(3′,2′-2,3)pyrone was recovered unchanged after being heated with hydroxylamine in ethanol for 22 hr.

α-(3-Phenyl-5-pyrazolyl)acetophenone hydrazone [10] was obtained when *sym*-dibenzoylacetone (0·3 g.) in methanol (15 ml.) was refluxed with 85% hydrazine hydrate (0·5 ml.) for 1 hr. It was isolated by dilution, crystallised from chloroform–light petroleum, and recrystallised from methanol in needles, m. p. and mixed m. p. 168° (Found: N, 20·2. Calc. for $C_{17}H_{16}N_4$: N, 20·3%).

6-Methyl-4,5-diphenyl-2-pyrone,[4] prepared from phenylacetone and ethyl phenylpropiolate, crystallised from methanol in cubes, m. p. 138° (Found: C, 82·3; H, 5·2. Calc. for $C_{18}H_{14}O_2$: C, 82·4; H, 5·4%).

cis-5-*Oxo*-3,4-*diphenylhex*-2-*enoic Acid*.—The last-mentioned pyrone (1·4 g.) was dissolved in warm 5% methanolic potassium hydroxide (30 ml.) and, when most of the methanol had been distilled off, the residue was diluted with water and extracted with ether. When the alkaline layer was acidified and extracted with ether, the *hexenoic acid* (1·2 g.) was recovered. It crystallised from benzene in needles, m. p. 170° (decomp.) (Found: C, 77·1; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·8%). With diazomethane, it gave the *methyl ester*, m. p. 102° (from light petroleum) (Found: C, 77·5; H, 6·3; OMe, 10·7. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2; OMe, 10·55%). This ester yielded the pyrone when mixed with an ethereal suspension of sodium ethoxide.

Attempted Fission of 6-*Benzyl*-4,5-*diphenyl*-2-*pyrone*.[4]—The pyrone (0·5 g.) was refluxed with 10% methanolic potassium hydroxide (20 ml.) for 30 min. The violet solution was then poured into water and extracted with ether which removed nothing. On acidification of the alkaline solution, the pyrone was recovered almost pure.

Methylation after Fission.—The pyrone (1·0 g.) was refluxed in 10% methanolic potassium hydroxide (30 ml.) for 30 min. and the solvent distilled. A solution of the residue in water (60 ml.) was treated (dropwise) with dimethyl sulphate (1·5 ml.), and the faintly alkaline mixture was then kept overnight; the methylation products (0·7 g.), m. p. 175°, separated. On crystallisation from benzene–light petroleum, substance " a " separated in elongated plates, m. p. 206° (Found: C, 85·1; H, 5·7%).

The first benzene–light petroleum liquor yielded on concentration substance " b," m. p.

[15] Ruhemann, *J.*, 1908, **93**, 431.
[16] Traverso, *Ann. Chim.* (*Italy*), 1957, **47**, 1244.

149°, which crystallised from ethanol in needles, m. p. 153° (Found: C, 85·0; H, 5·9; OMe, 16·7%).

5-*Methoxy*-4,6-*diphenyl*-2-*pyrone*.—Ethereal solutions of ω-methoxyacetophenone [17] (2·9 g., 1 mol.) and ethyl phenylpropiolate (3·5 g., 1 mol.) were successively added to an ice-cold suspension of sodium ethoxide (1·42 g., 1 mol.), and the mixture was kept at room temperature for 7 hr., then mixed with water. The ethereal solution was separated and the alkaline solution extracted with ether. The viscous oil (4·3 g.) recovered from the ethereal solution was kept overnight at room temperature, the *pyrone* (1·7 g., 31% yield), m. p. 110°, crystallising. It recrystallised from methanol in yellow prisms, m. p. 114° (Found: C, 77·6; H, 5·2; OMe, 11·3. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·1; OMe, 11·15%). The alkaline layer was acidified and extracted with ether, and the ethereal solution shaken with sodium hydrogen carbonate solution and then evaporated; a yellow viscous oil (0·4 g.) was recovered. The sodium hydrogen carbonate solution gave 1 g. of phenylpropiolic acid. The *picrate* crystallised from methanol and then light petroleum in needles, m. p. 105° (Found: C, 56·3; H, 3·3; N, 8·4. $C_{24}H_{17}O_{10}N_3$ requires C, 56·8; H, 3·4; N, 8·3%). It was hydrolysed to the pyrone by warm dilute aqueous-ethanolic ammonia.

cis-4-*Methoxy*-5-*oxo*-3 : 5-*diphenyl*-*pentenoic Acid*.—The foregoing pyrone (1·0 g.) was warmed with 5% methanolic potassium hydroxide (25 ml.), and most of the methanol was then distilled off. The residue was diluted with water and extracted with ether, and the alkaline solution acidified and extracted with ether. The *acid* (0·9 g.) recovered from the latter ethereal extract solidified on treatment with light petroleum. It crystallised from benzene–light petroleum in pale yellow plates, m. p. 115° (Found: C, 72·9; H, 5·4. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·45%). With diazomethane, it gave the *methyl ester*, pale yellow cubes, m. p. 90° (from light petroleum) (Found: C, 73·2; H, 5·8; OMe, 20·0. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·85; OMe, 20·0%). This ester was converted into the pyrone on treatment with sodium ethoxide in ether or with a few drops of 5% ethanolic potassium hydroxide.

5-*Methoxy*-4,6-*diphenyl*-2-*pyridone* was prepared when the foregoing pyrone (0·7 g.) was heated with 25% aqueous ammonia (4 ml.) for 2 hr. at 130—135°. The pyridone (0·6 g.), recovered after washing with water and cold methanol, crystallised from benzene–light petroleum in needles, m. p. 203°, which gave a red colour with ferric chloride (Found: C, 77·7; H, 5·7; N, 5·2. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·5; N, 5·05%).

1-*Hydroxy*-5-*methoxy*-4,6-*diphenyl*-2-*pyridone* was prepared when an ethanolic solution of the pyrone (1·0 g.) was heated for 20 hr. with hydroxylamine hydrochloride (1·0 g.) and sodium acetate (1·0 g.) in water (2 ml.). After dilution with water, the mixture was extracted with chloroform, and the solution was evaporated. The residue (1·0 g.) was treated with enough cold benzene to dissolve the unchanged pyrone, leaving the pyridone (0·35 g.), which crystallised from benzene–light petroleum in needles, m. p. 211°, giving a red colour with ferric chloride (Found: C, 73·8; H, 5·2; N, 4·7; OMe, 10·4. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·2; N, 4·8; OMe, 10·6%).

1-*Amino*-5-*methoxy*-4,6-*diphenyl*-2-*pyridone*.—A solution of the preceding pyrone (0·5 g.) in ethanol (30 ml.) was refluxed with 25% hydrazine hydrate (5 ml.) for 7 hr. The *pyridone*, m. p. 185°, separated on dilution and cooling. It crystallised from benzene–light petroleum in needles, m. p. 186° (Found: C, 74·15; H, 5·7; N, 9·6; OMe, 10·2. $C_{18}H_{16}O_2N_2$ requires C, 73·8; H, 5·5; N, 9·6; OMe, 10·6%). It gave an orange-red colour with ferric chloride, dissolved in dilute mineral acids, and reduced Fehling's solution and Tollens's reagent.

5-*Methoxy*-4,6-*diphenyl*-2-*thiopyrone*.—A solution of 5-methoxy-4,6-diphenyl-2-pyrone (1·0 g.) in benzene was boiled with phosphorus pentasulphide (2·5 g.) for 1 hr. The orange-red solution was then separated, and the residue washed with hot benzene. The combined filtrate and washings were shaken with ammonium sulphide, washed, dried, and evaporated. The red residue (1·0 g.) yielded the crude *thiopyrone*, m. p. 105°, on treatment with cold methanol. It crystallised from light petroleum–benzene in orange plates, m. p. 150° (Found: C, 73·2; H, 4·85; S, 11·0. $C_{18}H_{14}O_2S$ requires C, 73·5; H, 4·8; S, 10·9%). This thiopyrone was recovered unchanged after being heated with semicarbazide hydrochloride and sodium acetate in methanol for 10 hr.

When a solution of the thiopyrone (0·5 g.) in methanol (20 ml.) was refluxed with hydroxylamine hydrochloride (0·5 g.) and sodium acetate (0·5 g.) in water (2 ml.) for 1 hr., hydrogen sulphide was given off. On dilution and extraction with ether, 5-methoxy-4,6-diphenyl-2-pyrone, m. p. and mixed m. p. 114°, was isolated. The same pyrone was obtained when a

[17] Pratt and Robinson, *J.*, 1923, **123**, 748.

methanolic solution of the thiopyrone (0·3 g.) was refluxed with 25% hydrazine hydrate (4 ml.) for 5 min.

5-Methoxy-4-phenyl-6-p-tolyl-2-pyrone.—*ω-Methoxy-4-methylacetophenone* was prepared by stirring an ethereal solution of methoxyacetonitrile (21·0 g.) into *p*-tolylmagnesium bromide (from 8·8 g. of magnesium and 62 g. of *p*-bromotoluene) in ice-cold dry ether. The mixture was then kept at room temperature for 2 hr. and decomposed with ice and dilute sulphuric acid, and the ethereal solution separated, washed with sodium hydrogen carbonate solution, dried, and distilled. The residual oil was fractionally distilled and the fraction (15 g.) of b. p. 125—128°/3 mm. was redistilled at 127°/3 mm. (Found: C, 72·9; H, 7·4. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%). Its semicarbazone was prepared when an ethanolic solution of the ketone (0·5 g.) was refluxed with a solution of semicarbazide hydrochloride (0·5 g.) and sodium acetate (0·5 g.) in water (2 ml.) for 6 hr. After dilution and cooling, the mixture yielded the *semicarbazone* which crystallised from methanol in needles, m. p. 153° (Found: C, 59·5; H, 6·8; N, 19·1; OMe, 13·95. $C_{11}H_{15}O_2N_3$ requires C, 59·7; H, 6·8; N, 19·0; OMe, 14·0%).

5-Methoxy-4-phenyl-6-*p*-tolyl-2-pyrone was prepared by condensing ω-methoxy-4-methylacetophenone (3·3 g., 1 mol.) and ethyl phenylpropiolate (3·5 g., 1 mol.) in presence of sodium ethoxide (1·42 g., 1 mol.) as for the preceding homologue. The viscous oil (5·2 g.) recovered from the neutral ethereal solution yielded the *pyrone* (1·8 g., 31%), m. p. 142°, after being kept overnight. It crystallised from methanol in yellow needles, m. p. 143° (Found: C, 77·8; H, 5·5; OMe, 10·5. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5; OMe, 10·6%). A non-acidic yellow oil (0·7 g.) and phenylpropiolic acid (0·8 g.) were recovered from the alkaline solution. It failed to give a picrate or react with hydroxylamine when refluxed for 33 hr.

cis-4-*Methoxy-5-oxo-3-phenyl-5-p-tolylpentenoic acid* was prepared by the action of 5% methanolic potassium hydroxide on 5-methoxy-4-phenyl-6-*p*-tolyl-2-pyrone as described above and crystallised from benzene–light petroleum in pale yellow prisms, m. p. 141° (Found: C, 73·7; H, 5·9. $C_{19}H_{18}O_4$ requires C, 73·6; H, 5·8%). Its *methyl ester* formed pale yellow cubes, m. p. 65°, from light petroleum (Found: C, 73·8; H, 6·3; OMe, 19·0. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2; OMe, 19·1%). This ester gave the pyrone on treatment with basic reagents as above.

5-Methoxy-4-phenyl-6-p-tolyl-2-pyridone.—This was prepared when the foregoing pyrone (0·5 g.) was heated with 25% aqueous ammonia in a sealed tube for 2 hr. at 160—165°. The crude *pyridone* (0·5 g.) was freed from a resin by washing it with cold acetone. It crystallised from benzene–light petroleum in yellowish white needles, m. p. 228°, which gave a red colour with ferric chloride (Found: C, 77·85; H, 5·9; N, 4·8. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9; N, 4·8%).

1-*Amino-5-methoxy-4-phenyl-6-p-tolyl-2-pyridone.*—This *pyridone* was prepared by heating an ethanolic solution of the pyrone with 25% hydrazine hydrate for 7 hr. and crystallised from benzene–light petroleum in plates, m. p. 174°, which gave the characteristic reactions of 1-amino-2-pyridones (Found: C, 74·5; H, 6·0; N, 9·1; OMe, 9·9. $C_{19}H_{18}O_2N_2$ requires C, 74·5; H, 5·9; N, 9·15; OMe, 10·1%).

5-Methoxy-4-phenyl-6-p-tolyl-2-thiopyrone.—This *thiopyrone* was prepared by the action of phosphorus pentasulphide on 5-methoxy-4-phenyl-6-*p*-tolyl-2-pyrone as before and crystallised from benzene–light petroleum in orange plates, m. p. 165° (Found: C, 74·1; H, 5·1; S, 10·4; OMe, 10·05. $C_{19}H_{16}O_2S$ requires C, 74·0; H, 5·2; S, 10·4; OMe, 10·1%). It was hydrolysed to 5-methoxy-4-phenyl-6-*p*-tolyl-2-pyrone when heated with hydroxylamine or 25% hydrazine hydrate, but recovered unchanged after being heated with semicarbazide.

5-Methoxy-6-p-methoxyphenyl-4-phenyl-2-pyrone.—ω,4-Dimethoxyacetophenone (3·6 g., 1 mol.) and ethyl phenylpropiolate (3·5 g., 1 mol.) were condensed with sodium ethoxide as before. The viscous oil (6·3 g.) recovered from the neutral ethereal solution deposited the *pyrone* (2 g., 24%), m. p. 146°, when kept overnight at room temperature. It crystallised from ethanol in yellow needles, m. p. 148°, which did not form a picrate and was recovered unchanged after being heated with hydroxylamine for 40 hr. (Found: C, 74·1; H, 5·2; OMe, 19·95. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%).

cis-4-*Methoxy*-5-p-*methoxyphenyl-5-oxo-3-phenylpentenoic Acid.*—This *acid* was prepared by alkaline fission of 5-methoxy-6-*p*-methoxyphenyl-4-phenyl-2-pyrone and crystallised from benzene–light petroleum in cubes, m. p. 123° (Found: C, 69·9; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·95; H, 5·6%). A crystalline ester could not be obtained by the action of diazomethane on the acid, but the oily product yielded the pyrone on treatment with sodium ethoxide.

5-*Methoxy*-6-p-*methoxyphenyl*-4-*phenyl*-2-*pyridone*.—This was prepared when the above pyrone (0·5 g.) was heated with 25% aqueous ammonia (4 ml.) for 2 hr. at 160—165°. The *pyridone* (0·5 g.), m. p. 188—195°, was washed with cold acetone and crystallised from benzene–light petroleum in yellow plates, m. p. 206°, which gave a red colour with ferric chloride (Found: C, 74·35; H, 5·5; N, 4·65. $C_{19}H_{17}O_3N$ requires C, 74·3; H, 5·6; N, 4·6%).

1-*Amino*-5-*methoxy*-6-p-*methoxyphenyl*-4-*phenyl*-2-*pyridone* was prepared by the action of 25% hydrazine hydrate on the pyrone and crystallised from dilute methanol in needles, m. p. 148°, which gave the reactions of 1-amino-2-pyridones (Found: C, 70·55; H, 5·7; N, 8·7. $C_{19}H_{18}O_3N_2$ requires C, 70·8; H, 5·6; N, 8·7%).

5-*Methoxy*-6-p-*methoxyphenyl*-4-*phenyl*-2-*thiopyrone* was prepared from the foregoing pyrone and crystallised from benzene–light petroleum in orange-red needles, m. p. 174° (Found: C, 70·6; H, 5·0; S, 9·5; OMe, 18·5. $C_{19}H_{16}O_3S$ requires C, 70·4; H, 5·0; S, 9·9; OMe, 19·1%). It was hydrolysed to 5-methoxy-6-*p*-methoxyphenyl-4-phenyl-2-pyrone by hydroxylamine or hydrazine hydrate, but recovered unchanged from semicarbazide.

5-*Methoxy*-4,6-*di*-p-*methoxyphenyl*-2-*pyrone*.—ω,4-Dimethoxyacetophenone (3·6 g., 1 mol.) and ethyl *p*-methoxyphenylpropiolate (4·1 g., 1 mol.) were condensed in the presence of sodium ethoxide (1·42 g., 1 mol.) at room temperature and the mixture was kept for 10 hr. The yellow oil (5·7 g.) recovered from the neutral ethereal solution yielded the *pyrone* (0·8 g.), m. p. 146°, when kept overnight. It crystallised from ethanol in yellow prisms, m. p. 150°, which did not give a picrate (Found: C, 71·1; H, 5·3; OMe, 27·2. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·4; OMe, 27·5%).

5-*Methoxy*-4,6-*di*-p-*methoxyphenyl*-2-*thiopyrone* was prepared therefrom and crystallised from benzene–light petroleum in red prisms, m. p. 183° (Found: C, 68·1; H, 5·3; S, 8·7. $C_{20}H_{18}O_4S$ requires C, 67·8; H, 5·1; S, 9·0%).

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