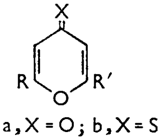
888. *4-Pyrones. Part III.* Reactions of Some 2,6-Disubstituted 4-Pyrones and Thiopyrones Involving the Carbonyl or Thiocarbonyl Group.*

By Mohamed A.-F. Elkaschef and Michael H. Nosseir.

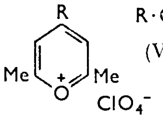
2,6-Disubstituted 4-pyrones react with Grignard reagents to give 1,3,5-trisubstituted pent-2-ene-1,5-diones. The thiopyrones, when treated with Grignard reagents or diazoalkanes, give ethylenic compounds and, when oxidised, give pyrones.

Gomberg and Cone[1] found that 2,6-dimethyl-4-pyrone did not react with phenylmagnesium bromide, a result that we have confirmed. Baeyer and Piccard,[2] however, using methyl- and phenyl-magnesium halides with perchloric acid obtained 2,4,6-trimethyl- and 2,6-dimethyl-4-phenyl-pyranium perchlorate (V), which they hydrolysed in water to the open-chain diketones (VIa and b). We have found that 2,6-diphenyl-4-pyrone with phenyl- or *p*-methoxyphenyl-magnesium bromide gives, after hydrolysis, the corresponding diketones (VIc and d). We postulate the mechanism of this reaction as illustrated. The positive charge being located more at position 2, the hydrolysis takes place at this position to give 1,3,5-trisubstituted pent-2-ene-1,5-diones (VI). This is

	R	R′
(I)	Me	Me
(II)	Ph	Ph
(III)	$C_6H_4{\cdot}OMe\text{-}p$	$C_6H_4{\cdot}OMe\text{-}p$
(IV)	Ph	$C_6H_4{\cdot}OMe\text{-}p$



a, X = O; b, X = S



(V) R = Me or Ph

$R{\cdot}CO{\cdot}CH{=}CR'{\cdot}CH_2{\cdot}COR$

(VI) a, R = R′ = Me
b, R = Me, R′ = Ph
c, R = R′ = Ph
d, R = Ph, R′ = $C_6H_4{\cdot}OMe\text{-}p$

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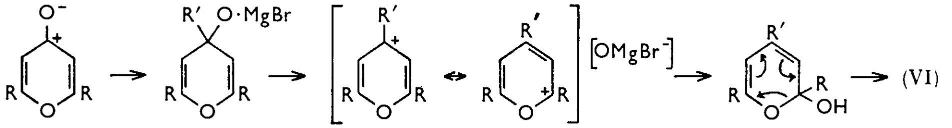
* Part II, *J.*, 1963, 440.

[1] Gomberg and Cone, *Annalen*, 1910, **376**, 277.

[2] Baeyer and Piccard, *Annalen*, 1911, **384**, 208.

supported by the gradual deepening of the colour of the mercuric chloride compounds of the 2,6-diphenyl-4-thiopyrones in the order (IIb, IVb, IIIb), the resonance being extended to the two extremities of the molecule (cf. Experimental section and ref. 12).



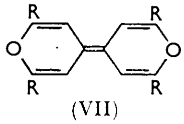
2,6-Diphenyl-4-thiopyrones (IIb), on the other hand, with phenylmagnesium bromide (filtered solution to avoid reaction due to residual metallic magnesium) afforded 2,2′,6,6′-tetraphenyl-4,4′-dipyranylidene (VIIa) (cf. the formation of dixanthylidene[4]). 2,6-Di-(*p*-methoxyphenyl)-4-thiopyrone (IIIb) on similar treatment afforded the 4-pyrone (IIIa).

Although 2,6-diphenyl-4-thiopyrones (IIb) gave 2,2′,6,6′-tetraphenyl-4,4′-dipyranylidene (VIIa) on fusion,[5] we have found that 2,6-di-(*p*-methoxyphenyl)-4-thiopyrone (IIIb) is recovered unchanged on similar treatment in an inert atmosphere. This result is explicable on the basis of vinylogy: [6] the phenyl compound (IIb) is a vinylogue of thiobenzophenone which is unstable to heat, whereas 4,4′-dimethoxythiobenzophenone is thermostable.[7]

When we fused in air, the 2,6-di-(*p*-methoxyphenyl)-4-thiopyrone (IIIb) was oxidised to the pyrone (IIIa). Also, the thiopyrones (Ib—IVb) were converted into the pyrones (Ia—IVa) when warmed with hydrogen peroxide in acetic acid (in contrast, thiopyridones are oxidised to *N*-alkyl-anhydro-*N*-hydroxypyridine-*p*-sulphonic acids [8]).

Boiling 2,6-diphenyl- (IIb) and 2,6-di-(*p*-methoxyphenyl)-4-thiopyrone (IIIb) with copper bronze in xylene affords the dipyranylidenes (VIIa and b), the methoxyl groups having no influence on the ease of this reaction [9] and in spite of the fact that the conversion (IIIb $\longrightarrow$ VIIb) could not be affected thermally.[10]

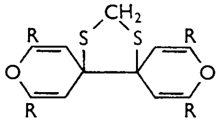
The dithio-analogue of 2,2′,6,6′-tetraphenyl-4,4′-dipyranylidene (VIIa) was recovered unchanged when fused with sulphur,[11] but fission of the ethylenic bond was effected by boiling this compound with thionyl chloride and subsequent dilution with water,[12] which gave the parent pyrone (IIa). The compound VIIb decomposes spontaneously, even at room temperature, but the products have not been identified.



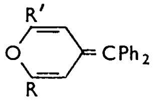
(VII)

a, R = Ph

b, R = $C_6H_4{\cdot}OMe$-*p*



(VIII)



(IX)

a, R = R′ = $C_6H_4{\cdot}OMe$-*p*

b, R = Ph, R′ = $C_6H_4{\cdot}OMe$-*p*

Whereas 2,6-diphenyl-4-thiopyrone with diazomethane gave a stable dithiole (VIII; R = Ph) which was converted into the ethylenic compound by the action of phenyllithium,[3] the methoxy-analogue gave the ethylenic compound (VIIb) directly, the dithiole

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[3] Schönberg, Elkaschef, Nosseir, and Sidky, *J. Amer. Chem. Soc.*, 1958, **80**, 6312.

[4] Schönberg, Rosenbach, and Schutz, *Annalen*, 1927, **454**, 37.

[5] Arndt, Scholz, and Nachtwey, *Ber.*, 1924, **57**, 1903.

[6] Schönberg, Sidky, and Aziz, *J. Amer. Chem. Soc.*, 1954, **76**, 5115.

[7] Staudinger and Freudenberger, *Ber.*, 1928, **61**, 1576.

[8] Elkaschef and Nosseir, *J. Amer. Chem. Soc.*, 1960, **82**, 4344.

[9] Schönberg, Schutz, and Nickel, *Ber.*, 1928, **61**, 1375.

[10] Mark, *Paper Trade J.*, 1941, **113**, 34; *Tech. Assoc. Papers*, 1941, **24**, 217.

[11] Schönberg and Askar, *J.*, 1942, 272.

[12] Elkaschef and Nosseir, *Egypt. J. Chem.*, 1959, **2**, 355; Nosseir, M.Sc. Thesis, Cairo University, 1957.

(VIII; R = C_6H_4·OMe-*p*) apparently affording thioformaldehyde and sulphur spontaneously.

Reaction of various thiopyrones with diazoalkanes has been reported to give sulphides which when heated alone[13] or with copper bronze[14] give ethylenic compounds. 2,6-Diphenyl-4-thiopyrone (IIb), however, afforded 4-diphenylmethylenepyran directly.[3] We find that 2,6-di-(*p*-methoxyphenyl)- and 2-*p*-methoxyphenyl-6-phenyl-4-thiopyrone with diphenyldiazomethane similarly afforded the ethylenic compounds (IXa and b) directly, whereas 2,6-dimethyl-4-thiopyrone (Ib) gave the pyrone (Ia) together with tetraphenylthiiran which may have originated by reaction of diphenyldiazomethane with thiobenzophenone formed in the same way as the thioformaldehyde mentioned above.

When treated with hydroxylamine, 2-*p*-methoxyphenyl-6-phenyl-4-thiopyrone afforded the oxime, a reaction previously observed by Arndt *et al.*[5] with 2,6-diphenyl-4-thiopyrone. 2,6-Di-(*p*-methoxyphenyl)-4-thiopyrone (IIIb), however, on such treatment, afforded the pyrone (IIIa); and 2,6-dimethyl-4-thiopyrone (Ib) gave, as well as 2,6-dimethyl-4-pyrone (Ia), a yellow compound previously obtained by Feist and Belart[15] by the action of hydroxylamine on heptane-2,4,6-trione. We shall report on the structure of this compound later.

EXPERIMENTAL

Light petroleum had boiling point 70—80°.

Reactions with Phenylmagnesium Bromide.—(*a*) *With* 2,6-*diphenyl*-4-*pyrone* (IIa). To a cold Grignard solution (from 3·2 c.c. of bromobenzene in 50 c.c. of ether), the pyrone (2·5 g.) in benzene (50 c.c.) was added. After 4 hours' refluxing, the mixture was left overnight, then decomposed with dilute hydrochloric acid and ice. The organic layer and an ethereal extract of the aqueous layer were united, washed, dried, and evaporated. The residual oil solidified under ether–light petroleum (yield 0·7 g.) and from light petroleum gave pale yellow crystals of 1,3,5-triphenylpent-2-ene-1,5-dione, m. p. and mixed m. p. 124° (lit.,[16] 119°) (Found: C, 84·8; H, 5·5. Calc. for $C_{23}H_{18}O_2$: C, 84·6; H, 5·6%). With concentrated sulphuric acid this gives a yellow-orange colour with a blue fluorescence and with sodium hydroxide a red colour.

With hydroxylamine hydrochloride and sodium acetate in ethanol, this product afforded the dioxime,[17] m. p. and mixed m. p. 145° (from light petroleum) (Found: C, 77·9; H, 5·7; N, 7·9. Calc. for $C_{23}H_{20}N_2O_2$: C, 77·5; H, 5·7; N, 7·9%).

(*b*) *With* 2,6-*dimethyl*-4-*pyrone*. The pyrone (Ia) treated as above gave back the starting pyrone, m. p. and mixed m. p. 132°.

(*c*) *With* 2,6-*diphenyl*-4-*thiopyrone* (IIb). To a cold filtered solution of phenylmagnesium bromide (from 5·3 c.c. of bromobenzene) in ether (50 c.c.), the thiopyrone (1 g.) in benzene was added. The mixture was refluxed for 15 hr. On cooling, deep red crystals separated and they were filtered off. The filtrate was worked as before, more of the red crystals being obtained. The total material (0·26 g.), crystallised from xylene, had m. p. 313° alone or mixed with 2,2′,6,6′-tetraphenyl-4,4′-dipyranylidene.[5]

(*d*) *With* 2,6-*di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb). This thiopyrone (1 g.) with a Grignard solution as above afforded the pyrone (IIIa), m. p. and mixed m. p.[3] 190°.

Action of p-*Methoxyphenylmagnesium Bromide on* 2,6-*Diphenyl*-4-*pyrone* (IIa).—A Grignard solution [from *p*-bromoanisole (5·2 g.)] and 2,6-diphenyl-4-pyrone (IIa) was carried as above with 5 hours' refluxing. After decomposition with cold dilute sulphuric acid, the mixture was steam-distilled and extracted with ether. The extract, on evaporation, gave a solid (0·8 g.) that from ethanol afforded pale yellow 3-*p*-methoxyphenyl-1,5-diphenylpent-2-ene-1,3-dione m. p. and mixed m. p. 128° (lit.,[18] 122°), giving an orange colour with concentrated sulphuric acid (Found: C, 80·8; H, 5·7. Calc. for $C_{24}H_{20}O_3$: C, 80·9; H, 5·6%). The *dioxime* had m. p. 158° (from light petroleum) (Found: C, 74·5; H, 5·6; N, 7·2. $C_{24}H_{22}N_2O_3$ requires C, 74·6; H, 5·7; N, 7·3%).

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[13] Staudinger and Siegwart, *Helv. Chem. Acta*, 1920, **3**, 833.
[14] Schönberg, Fateen, and Sammour, *J. Amer. Chem. Soc.*, 1957, **79**, 6020.
[15] Feist and Belart, *Ber.*, 1895, **28**, 1820.
[16] Dilthey, *J. prakt. Chem.*, 1916, **94**, 72.
[17] Dilthey, *J. prakt. Chem.*, 1917, **95**, 111.
[18] Dilthey and Taucher, *Ber.*, 1920, **53**, 252.

Action of Heat on 2,6-*Di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb).—The thiopyrone was fused at 230—240° under dry carbon dioxide for 15 min., then washed with aqueous ammonium sulphide, and crystallised from ethanol, giving the starting thiopyrone, m. p. and mixed m. p.[13] 180°. This reaction when carried in air afforded the pyrone (IIIa), m. p. and mixed m. p.[13] 190°.

Action of Hydrogen Peroxide on the 2,6-*Disubstituted* 4-*Thiopyrones*.—A solution of each of the thiopyrones (Ib—IVb) (0·5 g.) in acetic acid (30 c.c.) was heated with 30% hydrogen peroxide (5 c.c.) for ½ hr. on the water-bath. The solids that remained after evaporation of the solvent were crystallised and shown by m. p.s and mixed m. p.s to be the corresponding pyrones (I—IVa).

Action of Copper Bronze.—(*a*) *On* 2,6-*diphenyl*-4-*thiopyrone* (IIb). A solution of the thiopyrone (0·5 g.) in dry xylene (40 c.c.) was refluxed with copper bronze (5 g.) for 6 hr., then filtered while hot and the solid that separated on cooling (0·23 g.) was recrystallised from xylene, to give 2,2′,6,6′-tetraphenyl-4,4′-dipyranylidene, m. p. and mixed m. p.[5] 313°.

(*b*) *On* 2,6-*di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb). This compound (0·25 g.), when treated as above with copper bronze (2 g.), afforded 2,2′,6,6′-tetra-(*p*-methoxyphenyl)-4,4′-dipyranylidene (0·1 g.), m. p. and mixed m. p. 271°.

Cleavage of the Double Bond in Dipyranylidenes.—(*a*) 2,2′,6,6′-Tetraphenyl-4,4′-dipyranylidene when fused with sulphur in an inert atmosphere afforded the starting material.

(*b*) The red solution of the same compound (0·2 g.) in an excess of thionyl chloride (10 c.c.) was refluxed for 4 hr., then evaporated, and the remaining solid was dissolved in hot ethanol which was then diluted with much water. White crystals (0·1 g.) of the pyrone (IIa) were obtained which had m. p. and mixed m. p.[3] 140° (from ethanol).

On similar treatment, the methoxy-analogue (VIIb) gave decomposition products.

Action of Diazomethane on 2,6-*Di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb).—The thiopyrone (0·33 g.) in ether (30 c.c.) was treated with an excess of ethereal diazomethane, and set at 0° for 3 days and then at room temperature for the same period while a further amount of diazomethane solution was added each day. The total volume of the solution was 250 c.c. containing diazomethane generated from 30 g. of nitrosomethylurea. The oil that remained on removal of the ether was washed with light petroleum (b. p. $<50°$) and then with methanol; it solidified. This solid was boiled with ethanol and recovered after cooling. Recrystallised from benzene, it gave deep red 2,2′,6,6′-*tetra*-(p-*methoxyphenyl*)-4,4′-*dipyranylidene* (0·15 g.), m. p. 271° (no colour with concentrated sulphuric acid) (Found: C, 77·6; H, 5·5. $C_{38}H_{22}O_6$ requires C, 78·1; H, 5·5%).

Action of Diphenyldiazomethane.—*On* 2,6-*di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb). A solution of diphenyldiazomethane (from 3 g. of benzophenone hydrazone) in benzene (50 c.c.) was treated with the thiopyrone in benzene (25 c.c.), and the mixture was refluxed for 5 hr. and kept overnight at room temperature. The oily residue remaining on evaporation solidified under methanol (yield 0·3 g.) and, recrystallised from ethanol, gave yellow 4-*diphenylmethylene*-2,6-*di*-(p-*methoxyphenyl*)*pyran*, m. p. 210°, giving a yellow colour with a green fluorescence in concentrated sulphuric acid and in the solid state exhibiting a strong yellowish-green fluorescence in ultraviolet light (Found: C, 83·4; H, 5·7. $C_{32}H_{26}O_3$ requires C, 83·8; H, 5·7%).

(*b*) *On* 2-p-*methoxyphenyl*-6-*phenyl*-4-*thiopyrone* (IVb). This compound, treated with diphenyldiazomethane as above, afforded yellow 4-*diphenylmethylene*-2-p-*methoxyphenyl*-6-*phenylpyran* (IXb) (0·4 g.), m. p. 133° (from ethanol), giving colour reactions and fluorescence as above (Found: C, 86·6; H, 6·1. $C_{31}H_{24}O_2$ requires C, 86·9; H, 5·6%).

(*c*) *On* 2,6-*dimethyl*-4-*pyrone* (Ib). With diphenyldiazomethane this pyrone gave an oil that solidified under methanol and crystallised from ethanol. The product proved to be tetraphenylthiiran, m. p. and mixed m. p. 176° (Found: C, 85·6; H, 5·4; S, 8·7. Calc. for $C_{26}H_{20}S$: C, 85·7; H, 5·5; S, 8·8%). Evaporation of the methanol filtrate gave a solid that, crystallised from light petroleum, proved to be the dimethylpyrone.

Action of Diazofluorene on 2,6-*Di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb).—The pyrone (0·6 g.) and 9-diazofluorene (0·8 g.) were refluxed in benzene (50 c.c.) for 7 hr. and then kept overnight. The benzene was distilled off; the crystalline residue (0·32 g.), recrystallised from light petroleum, yielded red 4-9′-*fluorenylidene*-2,6-*di*-(p-*methoxyphenyl*)*pyran*, m. p. 224°, that gave a greenish-yellow colour with a green fluorescence in concentrated sulphuric acid (Found: C, 83·9; H, 5·4. $C_{32}H_{24}O_3$ requires C, 84·2; H, 5·3%).

Action of Mercuric Chloride on 2-p-*Methoxyphenyl*-6-*phenyl*-4-*thiopyrone* (IVb).—To the red solution of the thiopyrone in dry benzene at room temperature a few crystals of mercuric chloride were added. After some hours the surface of the crystals became yellowish-orange and the solution almost colourless.

Action of Hydroxylamine.—(*a*) *On* 2-p-*methoxyphenyl*-6-*phenyl*-4-*thiopyrone* (IVb). A mixture of the thiopyrone (0·3 g.) in ethanol (20 c.c.) with hydroxylamine hydrochloride (0·14 g.) and sodium acetate (1 g.) in water (1 c.c.), was refluxed for 3 hr. The solid product (0·2 g.) that separated on dilution with water crystallised from ethanol, to give the pale yellow 4-*pyrone oxime*, m. p. 178° (Found: N, 5·0. $C_{18}H_{15}NO_3$ requires N, 4·8%). The *picrate* of this oxime, formed from ethanolic solution and crystallised from ethanol, melted at 195° (Found: N, 10·2. $C_{24}H_{18}N_4O_{10}$ requires N, 10·7%).

(*b*) *On* 2,6-*di*-(p-*methoxyphenyl*)-4-*thiopyrone* (IIIb). Treating this pyrone as above afforded 2,6-di-(*p*-methoxyphenyl)-4-pyrone (IIIa), m. p. and mixed m. p.[3] 190° (Found: C, 73·6; H, 5·2. Calc. for $C_{19}H_{16}O_4$: C, 74·0; H, 5·2%) [*picrate*; m. p. 217° (from ethanol) (Found: C, 56·4; H, 3·7; N, 7·8. $C_{25}H_{19}N_3O_{11}$ requires C, 55·9; H, 3·5; N, 7·8%).

(*c*) *On* 2,6-*dimethyl*-4-*pyrone* (Ia) *and -thiopyrone* (Ib). This pyrone or thiopyrone, on reaction as above, and evaporation of the solvent, gave a solid that crystallised from water in yellow crystals, that resisted hydrolysis with hydrochloric acid and had m. p. 244° alone or mixed with the product[13] obtained by the reaction between heptane-2,4,6-trione and hydroxylamine hydrochloride (Found: N, 18·5. Calc. for $C_7H_{10}N_2O_2$: N, 18·2%).

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