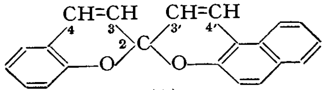
485. *Preparation of* spiro*Pyrans Derived from* 9-*Methyl- and* 9-*Ethylthiaxanthylium and* 9-*Benzylxanthylium Salts. The Action of Grignard Solutions on Thermochromic* spiro*Pyrans.*

By Ahmed Mustafa.

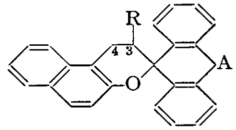
(*a*) *spiro*Pyrans (II*a*—II*c*) derived from 9-methyl- and 9-ethyl-thiaxanthylium and 9-benzylxanthylium salts have been prepared. These *spiro*pyrans are compared with benzo-β-naphtho*spiro*dipyran (I).

(*b*) The action of various Grignard solutions on thermochromic *spiro*pyrans (II*a* and V) leads to formation of 2 : 3-dihydrofuran derivatives (IV and VI).

(*a*) Dickinson and Heilbron (*J.*, 1927, 1699) have shown that only *spiro*pyrans having at least one of the pyran rings attached to a naphthalene nucleus form coloured ions when heated; further, that the 3′-carbon atom in the naphthopyran ring must be unsubstituted (cf. I). A study has now been made of the condensation of 9-methyl- and 9-ethyl-thiaxanthylium chloride and 9-benzylxanthylium chloride with 2-naphthol-1-aldehyde and of the *spiro*pyrans produced on hydrolysis (cf. Irving, *J.*, 1929, 1093), in order to compare the latter compounds with benzo-β-naphtho*spiro*dipyran (I). β-*Naphthothiaxantho*spiro*pyran* (II*a*, A = S) fulfils the above conditions and, as was expected, develops a pink colour when boiled with diphenyl ether and also when melted; in both cases the colour disappears on cooling. On the other hand, 3-*methyl-β-naphthothiaxanthos*piro*pyran* (II*b*) and 3-*phenyl-β-naphthoxanthos*piro*pyran* (II*c*), which are analogous to 3′-methyl- and 3′-phenyl-benzo-β-naphtho*spiro*dipyran, respectively, fail to give a colour on heating (cf. Mustafa, *Chem. Reviews*, 1948, **43**, 509).



(I.)

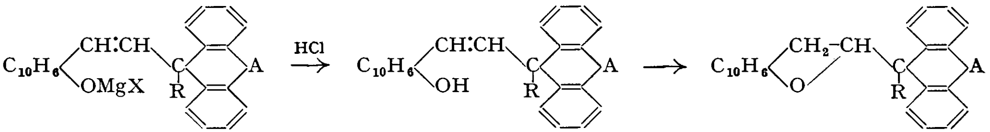


(II*a*; R = H; II*b*; R = Me, A = S; II*c*; R = Ph, A = O.)

The *spiro*pyrans themselves are reconverted into the corresponding thiaxanthylium or xanthylium salts only with difficulty; they give thiaxanthylium and xanthylium salt colorations, not with glacial acetic acid, but only when trichloroacetic acid is used.

(*b*) Recently, Schönberg, Mustafa, and Asker (*J.*, 1947, 847) have investigated the action of Grignard solutions on the thermochromic *spiro*pyrans, followed by hydrolysis, and found that the reaction led to the formation of 2 : 3-dihydrofuran derivatives. This reaction has been further extended, and the action of various Grignard solutions on (II*a*; A = S) and (II*a*; A = O) was studied. Similarly, the reaction leads to the formation of the 2 : 3-dihydrofuran *derivatives*

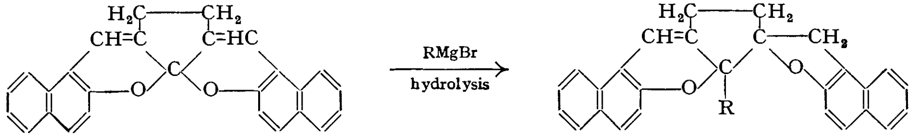
(II*a*) + R·MgX ⟶



(X = halogen.) (III.) (IV.)

(IV) and not of the phenolic compounds (III); (IV; R = Ph, A = S) is insoluble in aqueous alkali solution; it is not attacked by ethereal diazomethane or by benzoyl chloride in the presence of pyridine and is stable towards methyl sulphate in the presence of alkali. The diene reaction of (IV) with maleic anhydride was negative.

Similarly, the action of Grignard solutions on 3 : 3′-ethylenedi-β-naphtho*spiro*dipyran (V) leads to products which show properties analogous to those of (IV; R = Ph, A = S). These compounds are therefore formulated as (VI).



(V.) (VI.)

EXPERIMENTAL.

3-*Phenyl-β-naphthoxanthos*piro*pyran* (II*c*).—To a solution of 9-benzylxanthol (Decker, *Ber.*, 1905, **38**, 2493) (5 g.) in absolute ethyl alcohol (40 c.c.) was added 2-naphthol-1-aldehyde (6 g.), and a slow stream of dry hydrogen chloride gas was introduced. The yellow solution gradually darkened and reddish-brown crystals separated. After standing in the cold for 48 hours, the crystals were filtered off, and a suspension of these in acetone was hydrolysed by means of dilute aqueous ammonia, whereupon the crystals became colourless. The product was separated, washed with water, and crystallised from chloroform–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 240° (reddish-brown melt) (Found: C, 87·5; H, 4·6. $C_{31}H_{20}O_2$ requires C, 87·7; H, 4·7%). The spiro*pyran* (II*c*) is soluble in hot chloroform, but difficulty soluble in benzene. Its solution in diphenyl ether or tetralin is colourless, and it gives an orange-red colour with green fluorescence when treated with concentrated sulphuric acid.

*β-Naphthothiaxanthos*piro*pyran* (II*a*, A = S).—The theoretical quantity of 2-naphthol-1-aldehyde (6·5 g.) was added to a dry solution of 9-methylthiaxanthol in ether, prepared from thiaxanthone (10 g.) (Decker, *loc. cit.*), and a slow stream of dry hydrogen chloride gas was introduced. The yellow solution gradually changed to deep red with the separation of crystals, and was kept at 0° for 3 days; the crystals were filtered off, suspended in acetone, and treated with aqueous ammonia solution. The colourless solid obtained was filtered off, boiled with alcohol several times, and finally crystallised twice from benzene–light petroleum (b. p. 30—50°). The spiro*pyran* (II*a*; A = S) formed colourless crystals melting at 230° to a deep red liquid, becoming colourless again on solidification (Found: C, 82·3; H, 4·4; S, 8·5. $C_{25}H_{16}OS$ requires C, 82·4; H, 4·4; S, 8·8%). The solution of the compound in boiling xylene was colourless, but in boiling diphenyl ether or tetralin, a pink colour was obtained which disappeared on cooling. It gives a deep red colour changing to green after a few minutes when treated with concentrated sulphuric acid. It is difficulty soluble in boiling ethyl alcohol and light petroleum (b. p. 90—100°).

3-*Methyl-β-naphthothiaxantho*spiro*pyran* (II*b*).—Similarly, the theoretical quantity of 2-naphthol-1-aldehyde (6·5 g.) was added to a dry solution of 9-ethylthiaxanthol in ether, prepared from thiaxanthone (10 g.) and ethylmagnesium bromide (24·5 g.) (cf. Irving, *loc. cit.*), and a slow stream of hydrogen chloride was introduced. The yellow solution, which slowly became dark red with the separation of crystals, was kept in the cold for 48 hours; the crystals that separated were filtered off, washed with alcoholic ammonia solution, then with boiling acetone, and finally crystallised from xylene after the addition of light petroleum (b. p. 30—50°), forming colourless crystals, m. p. above 270° (red melt) (Found: C, 82·4; H, 4·5; S, 8·3. $C_{26}H_{18}OS$ requires C, 82·5; H, 4·7; S, 8·4%). The spiro*pyran* (II*b*) is soluble in benzene and xylene; its solution in boiling diphenyl ether is colourless and it gives a green solution in concentrated sulphuric acid.

*Action of Grignard Reagents on β-Naphthothiaxantho*spiro*pyran* (II*a*, A = S).—(i) *Phenylmagnesium bromide.* To an ethereal solution of phenylmagnesium bromide (prepared from magnesium, 0·9 g.; bromobenzene, 9 g.; dry ether, 50 c.c.), the *spiro*pyran (II*a*; A = S) (2 g.) and dry benzene (20 c.c.) were added. The mixture was heated under reflux for 2 hours, during which its colour changed from red through green to yellow; it was kept overnight, then decomposed with dilute hydrochloric acid, and extracted with ether. The ethereal solution was dried and evaporated, and the residue, after being washed several times with boiling light petroleum (b. p. 30—50°), was crystallised twice from alcohol, forming colourless crystals, m. p. 152° (colourless melt) [Found: C, 84·0; H, 4·8; S, 6·8; *M* (micro-Rast), 423. $C_{31}H_{22}OS$ requires C, 84·2; H, 5·0; S, 7·2%; *M*, 442]. 9-(2′ : 3′-*Dihydro-β-naphtho-2′-furyl*)-9-*phenylthiaxanthone* (IV; R = Ph, A = S) is readily soluble in benzene and xylene but dissolves with difficulty in light petroleum (b. p. 90—100°). It is insoluble in aqueous sodium hydroxide and dissolves with a pale yellowish-brown colour in concentrated sulphuric acid.

(ii) *Methylmagnesium iodide.* The *methyl* analogue (IV; R = Me, A = S) was similarly obtained by the action of methylmagnesium iodide on (II*a*, A = S) in colourless crystals from methyl alcohol, m. p. 128° (colourless melt) (Found: C, 82·0; H, 5·1; S, 7·9. $C_{26}H_{20}OS$ requires C, 82·1; H, 5·3; S, 8·4%). It is insoluble in aqueous sodium hydroxide and gives a yellow colour when treated with concentrated sulphuric acid.

*Action of Grignard Reagents on β-Naphthoxantho*spiro*pyran* (II*a*, A = O).—(i) *Phenylmagnesium bromide.* The *spiro*pyran (Irving, *loc. cit.*) was treated as described for (II*a*, A = S) with phenylmagnesium bromide. The colour of the reaction mixture changed from yellow to blue and finally pale yellow. The product was decomposed with dilute hydrochloric acid, extracted with ether, and the ether dried, and evaporated. The oily residue, when washed several times with light petroleum (b. p. 30—50°), formed a solid mass which after two crystallisations from benzene–light petroleum (b. p. 90—100°), gave colourless crystals, m. p. 126° (Found: C, 87·0; H, 5·2. $C_{31}H_{22}O_2$ requires C, 87·3; H, 5·2%). 2-(2′ : 3′-*Dihydro-β-naphtho-2′-furyl*)-2-*phenylxanthone* (IV; R = Ph, A = O) dissolves in benzene and hot ethyl alcohol, but is difficultly soluble in light petroleum (b. p. 90—100°) and insoluble in aqueous sodium hydroxide. It dissolves with a yellow colour in concentrated sulphuric acid.

(ii) *Methylmagnesium iodide.* The *methyl* analogue (IV; R = Me, A = O) was obtained by the action of methylmagnesium iodide on (II*a*; A = O) in colourless crystals, m. p. 121° (Found: C, 85·4; H, 5·3. $C_{26}H_{20}O_2$ requires C, 85·7; H, 5·5%), from ethyl alcohol. It is insoluble in aqueous sodium hydroxide, dissolves readily in hot benzene, and gives an orange-yellow colour with concentrated sulphuric acid.

Action of Grignard Reagents on 3 : 3′-*Ethylenedi-β-naphtho*spiro*dipyran* (V).—(i) *Phenylmagnesium bromide.* The *spiro*pyran (V) (Heilbron, Heslop, and Irving, *J.*, 1933, 430) (2 g.) was treated with phenylmagnesium bromide (prepared from magnesium, 0·9 g.; bromobenzene, 9·2 g.; dry ether, 50 c.c.) as mentioned above. The product was decomposed with dilute hydrochloric acid and extracted with ether, and the extract dried and evaporated. The crystals so obtained were washed several times with boiling light petroleum (b. p. 30—50°), then with hot benzene, and crystallised from xylene in colourless crystals, m. p. 269° (colourless melt) [Found: C, 87·4; H, 5·1; *M* (micro-Rast), 430. $C_{33}H_{24}O_2$ requires C, 87·6; H, 5·3%; *M*, 452]. 2-(2′ : 3′-*Dihydro-β-naphtho-2′-furyl*)-2-*phenyl*-2′ : 3-*ethylene-β-naphthopyran* (VI; R = Ph) dissolves in hot xylene but is difficultly soluble in boiling ethyl alcohol and ether and is insoluble in aqueous sodium hydroxide. It dissolves with an orange colour in concentrated sulphuric acid.

(ii) *α-Naphthylmagnesium bromide.* The *α-naphthyl* analogue (VI; R = α-$C_{10}H_7$) was obtained by the action of α-naphthylmagnesium bromide (prepared from α-bromonaphthalene, 10·2 g.; magnesium, 1·4 g.; dry ether, 50 c.c.) on (V) (2 g.) in colourless crystals, m. p. 260°, from xylene (Found: C, 88·2; H, 5·0. $C_{37}H_{26}O_2$ requires C, 88·4; H, 5·2%). It is insoluble in aqueous sodium hydroxide, dissolves in hot xylene, but with difficulty in ethyl alcohol, and gives a red colour with concentrated sulphuric acid.

FOUAD I UNIVERSITY, ABBASSIA-CAIRO, EGYPT.

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