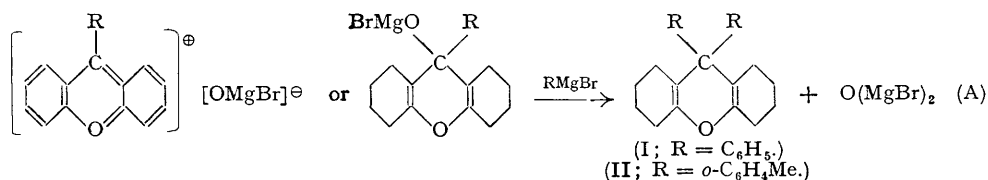


124. Action of Grignard Reagents. Part II.* Replacement of the Oxygen Atoms of Ketones by Two Hydrocarbon Radicals by the Action of Grignard Reagents.

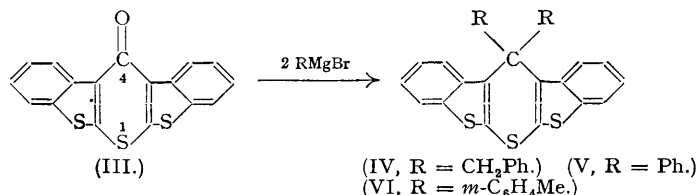
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It is shown that xanthone and the 1-thia- γ -pyrone derivative (III) react with Grignard reagents to form not only the carbinols, but also pyranones (see A), the oxygen atoms of the carbonyl groups being replaced by two hydrocarbon radicals; *e.g.*, xanthone yields with phenylmagnesium bromide 9:9-diphenylxanthen (I). 2:7-Dimethylxanthone (X) is easily obtained by the action of oxalyl chloride on di-*p*-tolyl ether.

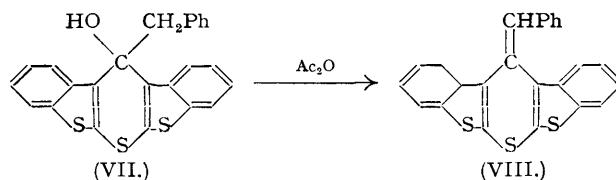
VERY little is known of the reaction indicated in the title. Ullmann and Engi (*Ber.*, 1904, **37**, 2367) have shown that when xanthone is treated with phenylmagnesium bromide, and the product hydrolysed, phenylxanthhydrol is formed, but a second compound related to xanthen is not recorded. We have found, however, that when the reaction mixture is evaporated to dryness, and then extracted with ligroin, the extract gives colourless 9:9-diphenylxanthen (I). A similar reaction was observed with *o*-tolylmagnesium bromide. We ascribe the formation of (I) to the salt-like nature of the primary reaction product.



In the above cases the carbinol, *e.g.*, phenylxanthhydrol, was the main product under our experimental conditions, and the second product, *e.g.*, (I), was obtained only in small yield; but when phenylmagnesium bromide or *m*-tolylmagnesium bromide was allowed to react on 2:3-6:5-dithionaphtheno-1-thia- γ -pyrone (III), 4:4-diphenyl- (V) and 4:4-di-*m*-tolyl-2:3-6:5-dithionaphtheno-1-thia- γ -pyran (VI) were obtained in good yield; in these two cases, the reaction mentioned in the title predominates. When (III) was treated

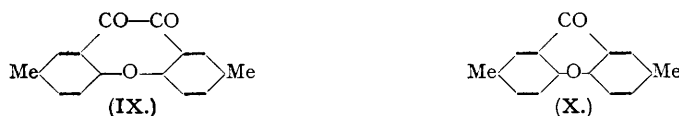


with benzylmagnesium chloride followed by hydrolysis, 4:4-dibenzyl- (IV) and 4-hydroxy-4-benzyl-2:3-6:5-dithionaphtheno-1-thia- γ -pyran (VII) were obtained, the former when a comparatively large amount of



benzylmagnesium chloride was used. The latter on treatment with acetic anhydride yielded the 4-benzylidene compound (VIII).

An Easy Method for Preparation of 2:7-Dimethylxanthone (X).—Schönberg and Aly Sina devised the following method. Oxalyl chloride was allowed to act on di-*p*-tolyl ether in the presence of aluminium chloride in the hope that (IX) might be synthesised. However, 2:7-dimethylxanthone (X) was obtained in a good yield. This reaction may be explained by the formation of carbonyl chloride by the action of aluminium chloride on oxalyl chloride (*cf.*, *inter alia*, Staudinger, *Ber.*, 1908, **41**, 3561).



EXPERIMENTAL.

9:9-Diphenylxanthen (I).—To an ethereal solution of phenylmagnesium bromide [prepared from magnesium (1.5 g.), bromobenzene (15 g.), and ether (40 c.c.)], xanthone (5 g.) and dry benzene (30 c.c.) were added. The mixture was refluxed for 5 hours and set aside overnight. The solvents were then distilled off on a water-bath, and the residue

* Schönberg and Moubasher (*J.*, 1944, 462) is regarded as Part I.

extracted several times with petrol (b. p. 50—60°). The extract was evaporated, and the residue steam distilled (to remove diphenyl). The residue crystallised from acetic acid in almost colourless crystals (0.5 g.), m. p. 199° undepressed on admixture with an authentic specimen (Ullmann and Engi, *loc. cit.*) (Found: C, 89.4; H, 5.4. Calc. for $C_{25}H_{18}O$: C, 89.8; H, 5.4%).

9:9-*Di-o-tolylxanthen* (II).—By an exactly analogous procedure *o*-tolylmagnesium bromide and xanthone gave colourless crystals which, recrystallised from alcohol, had m. p. 119° (Found: C, 90.1; H, 5.9. $C_{27}H_{22}O$ requires C, 90.0; H, 6.1%).

Action of Benzylmagnesium Chloride on 2:3-6:5-Dithionaphthene-1-thia- γ -pyrone (III).—(a) The pyrone (III) (see preceding paper) (1 g.) was treated with an ethereal solution of benzylmagnesium chloride, prepared from benzyl chloride (5.5 g.), magnesium (0.8 g.), and ether (30 c.c.), in the presence of dry benzene (20 c.c.) and refluxed for 5 hours. The yellow oil obtained after decomposition of the product with cold dilute hydrochloric acid was washed with ligroin (b. p. 30—50°) and then crystallised from ligroin (b. p. 100—110°) in almost colourless crystals, m. p. 176° (Found: C, 75.7; H, 4.83; S, 20.1. $C_{31}H_{22}S_3$ requires, C, 75.9; H, 4.5; S, 19.6%). 4:4-*Dibenzyl-2:3-6:5-dithionaphthene-1-thia- γ -pyran* (IV) dissolves in concentrated sulphuric acid with a yellow colour; it (0.3 g.) was recovered unchanged after refluxing for 3 hours with acetic anhydride (20 c.c.).

(b) The pyrone (2 g.) was treated similarly with the same amount of benzylmagnesium chloride as above. The yellowish-brown oil ultimately obtained was washed several times with ligroin (b. p. 30—50°), and 4-*hydroxy-4-benzyl-2:3-6:5-dithionaphthene-1-thia- γ -pyran* (VII) then crystallised from xylene after the addition of ligroin (b. p. 30—50°) in light yellow crystals, m. p. 220° (Found: C, 69.2; H, 3.55; S, 22.4. $C_{24}H_{16}OS_3$ requires C, 69.2; H, 3.8; S, 23.0%).

Action of acetic anhydride on (VII). The pyran (0.5 g.) was dissolved in acetic anhydride (20 c.c.), the solution refluxed for 3 hours, concentrated, and cooled, affording light yellow crystals, m. p. 244° (Found: C, 72.3; H, 3.7; S, 24.4. $C_{24}H_{14}S_3$ requires C, 72.4; H, 3.5; S, 24.1%), of 4-*benzylidene-2:3-6:5-dithionaphthene-1-thia- γ -pyran* (VIII), difficultly soluble in hot benzene.

Action of Arylmagnesium Bromides on (III).—(a) To an ethereal solution of phenylmagnesium bromide [from magnesium (0.9 g.), bromobenzene (9 g.), and dry ether (25 c.c.)], dry benzene (50 c.c.) and (III) (1 g.) were added. The mixture was refluxed, with stirring, for 5 hours, the ether being allowed to evaporate slowly. The substance dissolved completely to give an orange-yellow solution. The reaction mixture was kept overnight and then decomposed with cold water followed by dilute hydrochloric acid. The organic matter was extracted with ether, and the oil remaining after evaporation of the ether was washed with ligroin (b. p. 30—50°). The residue crystallised from ligroin (b. p. 100—110°) in yellow crystals, m. p. 235° (Found: C, 75.5; H, 4.1; S, 20.3. $C_{29}H_{18}S_3$ requires C, 75.4; H, 3.9; S, 20.7%). 4:4-*Diphenyl-2:3-6:5-dithionaphthene-1-thia- γ -pyran* (V) is freely soluble in benzene, gives no colour reaction with concentrated sulphuric acid, and contains no active hydrogen.

(b) 1 G. of (III) was treated with *m*-tolylmagnesium bromide (prepared from 9 g. of *m*-bromotoluene) as described above. The yellowish-brown oil obtained was washed with ligroin (b. p. 30—50°) and then with boiling alcohol. The remaining yellow solid was powdered and then crystallised from ligroin (b. p. 100—110°); after cooling and scratching, yellow crystals of 4:4-*di-m-tolyl-2:3-6:5-dithionaphthene-1-thia- γ -pyran* (VI) were obtained, m. p. 219° [Found: C, 75.9; H, 4.62; S, 19.6; *M* (micro-Rast), 488. $C_{31}H_{22}S_3$ requires C, 75.9; H, 4.5; S, 19.6%; *M*, 490]. The ligroin and the alcohol washings gave more product on slow evaporation. The pyran is freely soluble in benzene but difficultly in alcohol, and gives no colour with concentrated sulphuric acid.

2:7-*Dimethylxanthone* (X).—In a three-necked flask fitted with a mercury-sealed mechanical stirrer and a condenser, finely divided di-*p*-tolyl ether (10 g.) (Reilly, Drumm, and Barrett, *J.*, 1927, 67) was mixed with oxalyl chloride (25 g.), carbon disulphide (75 c.c.), and powdered anhydrous aluminium chloride (10 g.). The mixture was stirred first under ice-cooling for 2 hours, then after the addition of further 8 g. of aluminium chloride for another 4 hours, and finally left overnight. The solution was then acidified with dilute hydrochloric acid, the organic layer separated, and the carbon disulphide driven off on a water-bath. The residue was powdered, digested with hot 10% sodium carbonate solution until free acid was removed, washed with distilled water until free from sodium carbonate, dried on the pump, and then crystallised from alcohol. The 2:7-dimethylxanthone (X) had m. p. 143°; yield 80% (Found: C, 80.4; H, 5.54. Calc. for $C_{15}H_{12}O_2$: C, 80.4; H, 5.4%). For identification it was converted into 2:7:2':7'-tetramethyldixanthylen (Gurgenjanz and Kostanecki, *Ber.*, 1895, 28, 2311).