

245. *Reactions with Benzoxanthenes.*

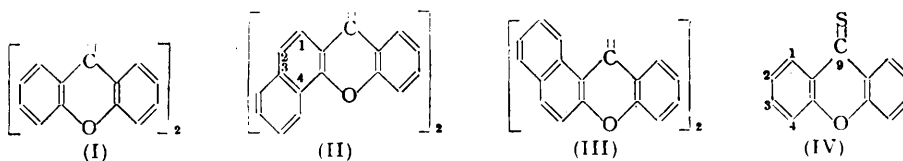
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The preparation and the thermochromic behaviour of di-3 : 4- and -1 : 2-benzoxanthylidenes (II) and (III) are discussed. These substances are cleaved by sulphur at 270° to 3 : 4- and 1 : 2-benzoxanth-9-thione, and by oxalyl chloride, followed by water, to the corresponding benzoxanthenes.

The action of phenylmagnesium bromide leads to 9-phenyl-3 : 4- and -1 : 2-benzoxanthhydrols, which on reduction yield 9-phenyl-3 : 4- and -1 : 2-benzoxanthenes.

Reduction of xanthenes and the corresponding thioketones with lithium aluminium hydride gives the corresponding methanes.

DIXANTHYLIDENE (I) is almost colourless at low temperatures, but becomes bluish-green when heated and its hot solutions, *e.g.*, in anisole, are bluish-green (Schönberg and Schütz, *Ber.*, 1928, **61**, 478). We have studied the thermochromic behaviour of di-3 : 4- (II) and -1 : 2-benzoxanth-9-ylidene (III) (*cf.* Mustafa and Hilmy, *Science*, 1952, in the press). The former is pale yellow at room temperature, and green when molten, gives a bluish-green solution in warm anisole and, in general, exhibits remarkable thermochromic behaviour. The isomer, which forms yellowish-green crystals, melts to an olive-green liquid; its solutions, *e.g.*, in anisole, are more weakly thermochromic to the unaided eye than are solutions of (II). With both substances the reversibility of the thermochromic phenomenon is the same as with dixanthylidene (*cf.* Schönberg, Ismail, and Asker, *J.*, 1946, 442).



The compounds (II) and (III) have been respectively obtained by the action of copper bronze on the 9 : 9-dichlorides from 3 : 4- and 1 : 2-benzoxanthone (*cf.* Schönberg and Asker, *J.*, 1942, 272) and by reduction of 3 : 4- and 1 : 2-benzoxanthone with zinc dust and acetic acid in the presence of concentrated hydrochloric acid (Gurgenjaz and Kostanecki, *Ber.*, 1895, **28**, 2310). The 3 : 4-benzo-compound has also been prepared by the action of copper bronze on 3 : 4-benzoxanth-9-thione (IV) (Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1375).

Substances (II) and (III) behave remarkably towards sulphur and with oxalyl chloride. When heated with sulphur, they form thioketones, the reaction with (II) occurring in a few minutes at 270° (for mechanism see Schönberg, Ismail, and Asker, *loc. cit.*). Treatment with oxalyl chloride, followed by water, breaks the ethylene bond, giving 3 : 4- and 1 : 2-benzoxanthone (*cf.* Schönberg and Asker, *loc. cit.*).

3 : 4- and 1 : 2-Benzoxanthone react with phenylmagnesium bromide in the usual manner, giving 9-phenyl-3 : 4- and -1 : 2-benzoxanthhydrol respectively. These hydrols are reduced readily by zinc dust and acetic acid to 9-phenyl-3 : 4- and -1 : 2-benzoxanthene; their photochemical behaviour towards oxygen will be discussed later.

Conover and Tarbell (*J. Amer. Chem. Soc.*, 1950, **72**, 3586) have shown that 4 : 4'-dimethoxybenzophenone and *NN*-dialkylaminobenzophenone gave a considerable amount of 4 : 4'-dimethoxydiphenylmethane and *NN*-dialkylaminodiphenylmethane respectively, on reduction with lithium aluminium hydride. Xanthenes, thioxanthone, and the two benzoxanthenes with excess of lithium aluminium hydride give good yields of the xanthenes.

EXPERIMENTAL

Di-3 : 4-benzoxanth-9-ylidene (II).—3 : 4-Benzoxanthone (2 g.) (Knapp, *J. pr. Chem.*, 1936, **146**, 116) was treated with oxalyl chloride (10 g.) (or with thionyl chloride, 15 c.c.) on a water-bath for 10 hours; the excess of oxalyl chloride was distilled off, and the residual orange oil

dissolved in dry xylene (30 c.c.) and refluxed with copper bronze (4 g.) for 6 hours with occasional shaking. The xylene solution was filtered hot and concentrated; on cooling, *di*-3:4-benzoxanth-9-ylidene separated in pale yellow crystals. It was filtered off, washed with cold acetone, and recrystallised from xylene; it (1.4 g.) had m. p. 346° (green melt), was sparingly soluble in boiling benzene and very sparingly so in absolute ethyl alcohol, and with concentrated sulphuric acid gave an orange-red colour [Found: C, 88.4; H, 4.2%; *M* (Rast), 450. $C_{34}H_{20}O_2$ requires C, 88.7; H, 4.35%; *M*, 460].

Reduction of 3:4-benzoxanthone (1 g.) with zinc dust (0.5 g.) and glacial acetic acid (10 c.c.) in the presence of concentrated hydrochloric acid (2—3 drops) gave *ca.* 0.05 g. of the same substance (identified by m. p. and mixed m. p. and thermochromic behaviour). This was also obtained by heating a mixture of copper bronze (2 g.) and 3:4-benzoxanth-9-thione (IV) (1 g.), in a stream of dry carbon dioxide, at 220° (bath-temp.) for 30 minutes. The xylene extract of the reaction mixture gave, on concentration, 0.5 g. of (II) (identified in the usual way).

Action of sulphur. The compound (II) (0.5 g.) was ground with sulphur (0.5 g.) and heated at 270° (bath-temp.) for 10 minutes, allowed to cool, powdered, and extracted repeatedly with light petroleum (b. p. 100—110°). The extract was concentrated, cooled, filtered from precipitated sulphur, further concentrated, and cooled. 3:4-Benzoxanth-9-thione crystallised in brown crystals, m. p. 140°, not depressed when mixed with a sample prepared as mentioned below.

Action of oxalyl chloride. The compound (II) (1 g.) was refluxed with oxalyl chloride (20 g.) for 6 hours, the excess of oxalyl chloride distilled off completely (pump), and the residual orange oil dissolved in benzene and shaken with water at 30° for 10 minutes. The benzene layer was evaporated and the residual pale yellow 3:4-benzoxanthone crystallised from benzene—light petroleum (b. p. 40—60°); it had m. p. 160° (Found: C, 82.8; H, 4.1. Calc. for $C_{17}H_{10}O_2$: C, 82.9; H, 4.1%) (m. p. and mixed m. p.); the mother-liquor also contained pure 3:4-benzoxanthone. The yield was almost quantitative.

Di-1:2-benzoxanth-9-ylidene (III).—This was prepared from 1:2-benzoxanthone (Graebe and Feer, *Ber.*, 1886, 19, 2612; Kostanecki, *Ber.*, 1892, 25, 1643) by the action of oxalyl chloride and copper bronze as described for the preparation of (II). It separated from the concentrated xylene solution, in yellowish-green crystals (*ca.* 75%), m. p. 290° (olive-green melt), soluble in hot xylene, difficultly soluble in alcohol and benzene. With concentrated sulphuric acid it gave an orange-red colour [Found: C, 88.5; H, 4.3%; *M* (Rast), 448. $C_{34}H_{20}O_2$ requires C, 88.7; H, 4.3%; *M*, 460]. It was also obtained, in *ca.* 15% yield, by the action of zinc dust and acetic acid in the presence of hydrochloric acid (*cf.* above).

Action of sulphur. 1:2-Benzoxanth-9-thione was obtained, by the action of sulphur on (III) as described in the case of (II), as green crystals (from benzene), m. p. 147° (m. p. and mixed m. p. with a sample prepared as described below).

Action of oxalyl chloride. The reaction was carried out as described in the case of (II) and the 1:2-benzoxanthone was obtained on crystallisation from benzene. It did not depress the m. p. of an authentic specimen (Graebe and Feer, *loc. cit.*).

3:4-Benzoxanth-9-thione.—The orange oil obtained by the action of oxalyl chloride (25 g.) on 3:4-benzoxanthone (5 g.), as described previously, was dissolved in dry benzene (40 c.c.) and refluxed for 6 hours with thiolacetic acid (8 c.c.), a deep green colour developing. The excess of benzene and acid was removed by distillation and, on addition of light petroleum (b. p. 40—60°) to the residue, 3:4-benzoxanth-9-thione was deposited in brown crystals (*ca.* 3.5 g.); recrystallised from benzene, it had m. p. 140—141° (Found: C, 77.6; H, 3.7; S, 12.2. $C_{17}H_{10}OS$ requires C, 77.9; H, 3.8; S, 12.2%). It dissolved in hot benzene to a greenish solution, was sparingly soluble in light petroleum and gave an orange-red colour with concentrated sulphuric acid. When mercuric chloride crystals were added to a dilute solution of it in benzene, they acquired a red-brown colour.

1:2-Benzoxanth-9-thione.—1:2-Benzoxanthone (4 g.), treated as above, gave this *thione* as dark green crystals (from benzene), m. p. 147° (green-melt) (*ca.* 2.6 g.) (Found: C, 77.7; H, 3.7; S, 12.1%). It was difficultly soluble in cold ether and soluble in concentrated sulphuric acid with a red colour. When the green solution of the substance in benzene was treated with mercuric chloride crystals, their colour changed immediately to red.

9-Phenyl-3:4-benzoxanthene.—To a Grignard solution of phenylmagnesium bromide [from magnesium (1.8 g.), bromobenzene (18 g.), and dry ether (75 c.c.)], dry benzene (40 c.c.) was added, and the mixture treated gradually with powdered 3:4-benzoxanthone (5 g.). The mixture was refluxed for 2 hours, set side overnight, poured into ice-cold, dilute hydrochloric acid, and extracted with ether, and the extract was dried and evaporated. The oily residue

solidified on storage and crystallised from benzene in colourless crystals, m. p. 230° (Found: C, 85.0; H, 4.7; active H, 0.29. $C_{23}H_{16}O_2$ requires C, 85.2; H, 4.9; active H, 0.31%). 9-Phenyl-3:4-benzoxanthhydrolyd gave an orange-yellow colour with concentrated sulphuric acid, and was soluble in hot benzene, but slightly soluble in cold ethyl alcohol. Its reduction was carried out as described by Ullmann and Engi (*Ber.*, 1904, 37, 2371) for 9-phenylxanthen by means of zinc dust and acetic acid with platinum chloride as a catalyst. 9-Phenyl-3:4-benzoxanthen recrystallised from light petroleum (b. p. 80—100°) in colourless crystals, m. p. 133—134°, soluble in benzene and giving no colour with concentrated sulphuric acid (Found: C, 89.3; H, 5.2. $C_{23}H_{16}O$ requires C, 89.6; H, 5.2%).

9-Phenyl-1:2-benzoxanthen.—9-Phenyl-1:2-benzoxanthhydrolyd, obtained as described above, crystallised from alcohol in colourless crystals, m. p. 175—176° (Found: C, 85.1; H, 4.8; active H, 0.30%) (Dilthey, Quint, and Dahm, *J. pr. Chem.*, 1934, 141, 75, gave for 9-phenyl-1:2-benzoxanthhydrolyd, m. p. 172—173°). Reduction, as described previously, gave 9-phenyl-1:2-benzoxanthen as colourless crystals (from benzene-ethyl alcohol), m. p. 169—170° (Found: C, 89.4; H, 5.2%); this gives no colour with concentrated sulphuric acid.

Reduction with Lithium Aluminium Hydride.—The reactions were carried out in solvents dried over sodium. A 250-c.c. three-necked flask fitted with a reflux condenser, mercury-sealed stirrer, and dropping funnel was used. To pulverised lithium aluminium hydride (0.5 g.) (from New Metals and Chemicals Ltd., London) was added ether (50 c.c.); stirring produced a milky suspension. After 15 minutes, 1 g. of the ketone or thioketone in benzene (40 c.c.) was added in portions. The reaction mixture was refluxed on a boiling water-bath for 3 hours with continuous stirring and then set aside overnight at room temperature. After addition to ice-cold water and treatment with aqueous ammonium chloride solution, the ethereal solution was washed with water, dried (Na_2SO_4), and evaporated; the reduction products are reported in the Table.

Reactant	Product *	Yield (%)	Reactant	Product *	Yield (%)
Xanthone	Xanthen	90	Michler's thioketone	Michler's methane ...	72
Thioxanthone	Thioxanthen	74	Xanthione	Xanthen	78
3:4-Benzoxanthone	3:4-Benzoxanthen ¹	85	Thioxanthione	Thioxanthen	83
1:2-Benzoxanthone	1:2-Benzoxanthen ²	82	3:4-Benzoxanth-9- thione	3:4-Benzoxanthen...	81

¹ M. p. 95—96° [from light petroleum (b. p. 60—80°)] (Found: C, 87.8; H, 5.1. Calc. for $C_{17}H_{12}O$: C, 87.9; H, 5.2%); red picrate, m. p. 126° (Found: C, 59.8; H, 3.2; N, 9.0. Calc. for $C_{17}H_{12}O, C_6H_3O_7N_3$: C, 59.9; H, 3.3; N, 9.1%) (Baddar and Gindy, *J.*, 1951, 231, have given for 3:4-benzoxanthen, m. p. 90—91°). ² Colourless (from alcohol), m. p. 99—100° [Found: C, 87.7; H, 5.0%; M (Rast), 227. Calc. for $C_{17}H_{12}O$: C, 87.9; H, 5.2%; M, 232] (Phomina, *Annalen*, 1890, 257, 89, gave for 1:2-benzoxanthen, m. p. 80°).

* The reduction products were identified by the m. p. and mixed m. p. with authentic specimens.