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674. Photodehydrogenation and Photo-oxidation of Some Thermochromic Ethylenes and Related Compounds.

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A new type of thermochromic ethylene (I) is photo-oxidised in presence of oxygen, giving anthraquinone and fluorenone; it is not affected by sunlight in a carbon dioxide atmosphere. In the early stages of the reaction a peculiar reversible colour change was achieved. On the other hand, a related compound (V) and a derivative (VI) are photodehydrogenated in presence of oxygen or carbon dioxide with the formation of highly condensed ringsystems.

THERMOCHROMISM and piezochromism exhibited by certain polynuclear ethylenes, *e.g.*, dianthraquinone and dixanthylidene, have been attributed to diradical formation ¹ or internal betaine structure.²

We here report a new thermochromic ethylene, 9-9'-fluorenylideneanthrone (I), a yellowish-brown solid (violet melt) which gives deep violet solutions that exhibit thermochromism. When pressed, the crystals change to deep violet (piezochromism). The fact that it suffers photo-oxidation with cleavage to anthraquinone and fluorenone (the first case of this type in thermochromic ethylenes) seems to favour the existence of a diradical whose formation is enhanced by irradiation. Acceleration of oxygen absorption with time

¹ Ingold and Marshall, J., 1926, 3080; Schönberg and Schütz, Ber., 1928, **61**, 478; Bergmann and Engel, Z. phys. Chem., 1930, **8**, B, 135; Bergmann and Corte, Ber., 1933, **66**, 39; Schönberg, Kaltschmidt, and Schulten, *ibid.*, 1933, **66**, 247; Bergmann, "Isomerism and Isomerisation of Organic Compounds," John Wiley and Sons, Inc., New York, 1948, p. 47; Grubb and Kistiakowsky, J. Amer. Chem. Soc., 1950, **72**, 419; Theilacker, Kortüm, and Friedheim, Ber., 1950, **83**, 508; Le Fèvre and Youhotsky, J., 1953, 1318.

² Schönberg, Ismail, and Asker, J., 1946, 442.

(Table) indicates that the compound is producing a fresh chain-starting catalyst (IIa or b) and forming a peroxide; although it was not isolated, its presence was revealed by the



peculiar reversible colour change which was noticed in the early stages of the photo-This colour change is more or less similar to that given by hexaphenylethane.³ oxidation.



Of several possible mechanisms for the photochemical cleavage by oxygen, reaction by way of the peroxide (IV) is favoured : the radical (IIb) supposed to be formed then, like (IIa), undergoes a similar chain reaction.

(IV) → Anthraquinone + Fluorenone + (IIb)

Photo-oxidation of the compound (I) is somewhat similar to the autoxidation of bisdiphenylene-ethylene⁴ and the photo-oxidation of polystyrene peroxide.⁵

The compound (I) was not affected by sunlight in a carbon dioxide atmosphere or in the dark in presence of oxygen; its photo-oxidation was inhibited in presence of ϕ -benzoquinone.⁴ On the other hand, 10-9'-thiaxanthylideneanthrone (V) and its Grignard



product, 9:10-dihydro-9-phenyl-10-10'-thiaxanthylideneanthran-9-ol (VI), were dehydrogenated on irradiation in either oxygen or carbon dioxide, yielding the benzo [a, o] perylenes (VII) and (VIII) respectively.

- ³ Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, 1953, p. 686. 4 Wittig and Pieper, Ber., 1940, 73, 295; Wittig, Annalen, 1941, 546, 142, 172; 1947, 558, 201, 218.
- ⁵ Miller and Mayo, J. Amer. Chem. Soc., 1956, 78, 1017; Mayo and Miller, ibid., p. 1023.

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The presence of one carbonyl group in compound (V) was ascertained by its reaction with phenylmagnesium bromide and lithium aluminium hydride, followed by hydrolysis in the usual manner, whereby the alcohol (VI) and 9': 10'-dihydro-10-9'-anthrylidene-thiaxanthen (IX) respectively were formed.

EXPERIMENTAL

9-9'-Fluorenylideneanthrone (1).—A powdered mixture of 9:9-dichlorofluorene⁶ (6 g.) and anthrone (5·4 g.) ⁷ was heated in a Pyrex glass tube (2·5 cm. diam.) in an ethyl phthalate bath. At 140° (bath-temperature) the solid began to melt and brisk evolution of hydrogen chloride occurred. The temperature was raised to about 160° for 2 hr., evolution of the gas nearly ceasing and the mass solidifying. The cooled mass was extracted with boiling xylene (20 c.c.), the filtrate cooled, and the yellowish-green solid was filtered off, triturated with ether, and dried (4 g.). From xylene-butanol it formed brownish-green crystals, m. p. 283— 284° (deep violet melt), giving a deep green colour with concentrated sulphuric acid, moderately soluble in benzene, toluene, and xylene, sparingly soluble in methyl and ethyl alcohol, to deep violet solutions. This *product* (I) shows reversible and pronounced thermochromic effects in very dilute solutions, *e.g.*, benzene (deep violet —> violet red, with fading). When pressed strongly with a glass pestle the crystals attained a permanent deep violet colour which changed back to brownish-yellow in presence of ether vapour (Found : C, 90·5; H, 4·6. C₂₇H₁₆O requires C, 91·0; H, 4·5%).

9': 10'-Dihydro-10'-hydroxy-10'-phenyl-10-9'-anthrylidenethiaxanthen (VI).—To a solution of phenylmagnesium bromide (magnesium, 0.73 g.; bromobenzene, 4.7 g.; dry ether, 20 c.c.), dry benzene (100 c.c.) was added and the mixture treated gradually with powdered 10-9'-anthronylidenethiaxanthen² (V) (3.9 g.). The mixture was refluxed (with stirring) for 4 hr., the ether being allowed to evaporate slowly; it assumed a deep red-violet colour. The cooled mixture was poured into ice-cold water acidified with hydrochloric acid. The solid (A) which separated was filtered off, and the benzene layer separated, washed, and evaporated. The residue was added to (A) and the whole material (4 g.) crystallised from toluene-light petroleum (b. p. 80—100°) as pale green prismatic needles, m. p. 280—281° (deep brown melt). This compound gave a reddish-brown colour with concentrated sulphuric acid, and was moderately soluble in benzene, toluene, and xylene, slightly soluble in ethyl alcohol (Found : C, 85.0; H, 4.8; S, 6.5. C₃₃H₂₂OS requires C, 85.0; H, 4.7; S, 6.9%).

9': 10'-Dihydro-10-9'-anthrylidenethiaxanthen (IX).—To pulverised lithium aluminium hydride (0.5 g.) was added dry ether (50 c.c.); stirring produced a milky suspension. After 15 min., the compound (V) (1 g.) in dry benzene (50 c.c.) was added gradually. The mixture was refluxed (with stirring) for 3 hr. and set aside overnight, then poured into ice-cold water acidified with hydrochloric acid, the solid (A) was filtered off, and the benzene layer separated, washed, dried, and evaporated. The residue was added to (A) and the whole *product* (0.65 g.) crystallised from toluene in fine prismatic needles, m. p. 306—308°, soluble in methyl and ethyl alcohols (Found : C, 86.5; H, 4.9; S, 8.6. C₂₇H₁₈S requires C, 86.6; H, 4.8; S, 8.6%).

Photochemical Experiments.—The following experiments were carried in Pyrex glass tubes (2.5 cm. diam.). The benzene used was thiophen-free and dried over sodium.

(a) 9-9'-Fluorenylideneanthrone (I).—The compound (1·15 g.) suspended in benzene (70 c.c.) (violet solution) was placed in direct sunlight (CaCl₂ guard-tube) for one month (April); a pale yellow solution was produced. It was concentrated to about 7 c.c., then cooled and the straw-yellow crystals were filtered off (0·3 g.). They crystallised from glacial acetic acid in pale yellow long needles, m. p. 285°, not depressed by admixture with anthraquinone. The original mother-liquor was subjected to several fractional crystallisations, till its volume was about 1 c.c. The different crops of crystals separated proved to be anthraquinone (total 0·5 g.). The residual orange mother-liquor was freed from benzene and the residual oil (0·45 g.) was distilled under a vacuum. The yellow distillate crystallised from benzene-light petroleum (b. p. 60—80°) in pale yellow needles, m. p. 84°, not depressed by admixture with fluorenone. The Table indicates the acceleration of oxygen absorption with time. After illumination in the dark or in carbon dioxide in presence of sunlight, no colour change occurred and the original material was recovered unchanged.

⁶ Smedley, J., 1905, 1249.

⁷ Meyer, Org. Synth., Coll. Vol. I, 1944, p. 60.

Jeffreys: Oxazole Cyanine and

Time (hr.)		1	2	3	4	5	6	9	11
$\Delta \phi$ (cm.)		0	0	0	0.1	0.3	0.6	2.0	3.6
Time (hr.)		11.5	12.0	13.0	14.0	14.5	15.0	16.0	17.0
Δp (cm.)	•••••	$4 \cdot 2$	5.0	5.5	$6 \cdot 2$	6.3	6.3	6.3	6.3

(b) 10-9'-Thiaxanthylideneanthrone (V). (i) The compound (1 g.), suspended in benzene (25 c.c.), sealed under carbon dioxide, was left in direct sunlight for 2 weeks (October); the solution became reddish-brown with a deep fluorescence, and on concentration to about 5 c.c. under reduced pressure afforded 16-oxo-7-thiadibenzo[a, o]perylene (VII) (0.8 g.); this crystallised from benzene in orange-red prismatic needles, m. p. 245° (Found : C, 83.8; H, 3.4; S, 8.2. $C_{27}H_{14}OS$ requires C, 83.9; H, 3.6; S, 8.3%), giving an intense green colour with concentrated sulphuric acid, sparingly soluble in cold or hot ethyl alcohol with an orange-red colour and a yellow fluorescence (more intense in the cold). It dissolved in cold benzene, toluene, or xylene with a deep yellowish-green fluorescence. When a drop of the benzene solution was put on a glazed white porcelain plate, it looked bright yellow without any red colour, but dried to orange-red crystals.

(ii) Experiment (a) was repeated with 0.2 g. suspended in benzene (20 c.c.) under a calcium chloride guard-tube. Irradiation was for one week (October). The reddish-brown solution obtained was concentrated and the crystalline product formed was filtered off (0.12 g.) and identified as (VII).

(c) 9': 10'-Dihydro-10'-hydroxy-10'-phenyl-10-9'-anthrylidenethiaxanthen (VI). (i) This compound (1 g.), suspended in benzene (50 c.c.), sealed under carbon dioxide, was left in direct sunlight for 12 days (October); the solution became green with a yellow fluorescence, and on concentration to about 5 c.c. under reduced pressure and cooling, afforded crystals of 16-hydroxy-16-phenyl-7-thiadibenzo[a, o]perylene (VIII) (0.7 g.); this crystallised from benzene-light petroleum (b. p. 60-80°) in orange crystals, m. p. 275°. It is moderately soluble in benzene, toluene, and xylene, sparingly soluble in ethyl alcohol (Found : C, 85.0; H, 4.4; S, 6.3. C₃₃H₂₀OS requires C, 85.4; H, 4.3; S, 6.9%).

(ii) Experiment (i) was repeated with 0.2 g. in 20 c.c. of benzene under a calcium chloride guard-tube, irradiation being for 5 days (October). The green solution obtained was concentrated and the crystalline product obtained was filtered off (0.1 g.) and identified as (VIII).

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