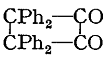
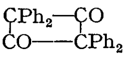
43. *The Constitution of the Dimeric Permanganate-coloured Diphenylketen.*

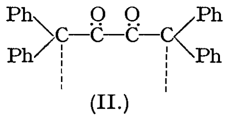
By Alexander Schönberg and Aly Sina.

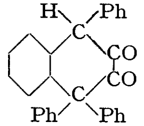
For the permanganate-coloured dimeric diphenylketen obtained by pyrolysis of benzilic acid, formula (IV) is advanced. The substance reacts with piperidine giving the colourless compound (V), which on heating is reconverted into piperidine and (IV).

Langenbeck and Langenbeck (*Ber.*, 1928, **61**, 938) have shown that when benzilic acid is heated in the presence of a small amount of anhydrous sodium carbonate or potassium benzilate, a permanganate-coloured crystalline substance, $C_{28}H_{20}O_2$, is obtained for which they advanced formula (I), *i.e.*, that of a dimeric diphenylketen. Formula (I*a*) was proposed by Staudinger (*Ber.*, 1911, **44**, 523) for a colourless dimeric isomer.


(I.)


(I*a*.)

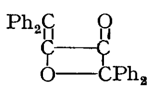

(II.)

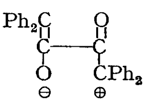

(III.)

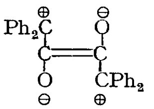
According to its discoverers (*loc. cit.*), 1 mol. of the permanaganate-coloured substance on oxidation yielded more than one mol. of benzophenone, but no crystalline derivative could be obtained by treatment with alcoholic potash, alcoholic potassium cyanide, phosphorus pentachloride, thionyl chloride, alcoholic bromine, zinc dust and acetic acid, ethylmagnesium bromide, or phenylhydrazine, and with *o*-phenylenediamine it failed to give a quinoxaline. The most remarkable property of the substance is its visible colour, the intensity of which greatly exceeds that of diacetyl, benzil, or phenanthraquinone and is of the order of that of dyes.

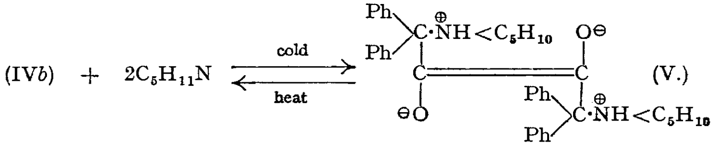
Formula (I) was challenged by Wittig and Lupin (*Ber.*, 1928, **61**, 1630), who proposed the diradical formula (II), but this was highly improbable because the substance is very stable towards oxygen, and was finally disproved by investigation of the magnetic properties (Müller, *Ber.*, 1935, **68**, 1883). Schlenk ("Ausführliches Lehrbuch der organischen Chemie," Vol. II, p. 521, Vienna, 1939) therefore advanced formula (III), although without any experimental evidence, but this has to be discarded for the following reasons. (i) Its structure as a cyclic 1 : 2-diketone cannot explain the intensity of the absorption in the visible part of the spectrum (cf. the absorption of camphorquinone, phenanthraquinone, and acenaphthenequinone). (ii) The compound does not give a quinoxaline derivative; this cannot be explained by enolisation, for we find that the substance has no active hydrogen; also zinc-dust distillation yields no crystalline substance except diphenylmethane, whereas (III) should yield naphthalene or its phenyl derivatives. (iii) Formula (III) is inconsistent with the production of more than 1 mol. of benzophenone per mol. of compound on oxidation (see above).

For the dimer in question, which has possibilities of resonance, we propose formula (IV), (IV*a*), or (IV*b*). The last explains the action of piperidine, in which the compound dissolves to give, after some time, an almost colourless solution, from which colourless crystals are obtained which have the nature of an ammonium derivative; on heating, they regenerate their components. The disappearance of colour on formation of the *salt* (V) is explained by the fact that the chromophore, namely, the positively charged carbon atom, is no longer present.


(IV.)

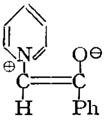

(IV*a*.)

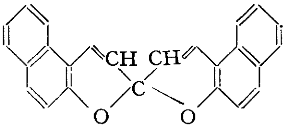

(IV*b*.)

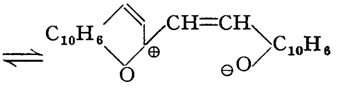

(V.)

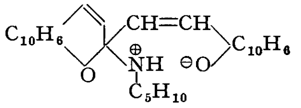
According to (IV*a*) and (IV*b*), the dimer is a *C*-enol betaine, *i.e.*, one in which the positive charge is on the carbon atom and not on the nitrogen atom, as it is in the *N*-enol betaines [cf. (VI); Kröhnke, *Ber.*, 1935, **68**, 1178].

The strongly coloured dimer is an analogue of the coloured forms of the *spiro*dinaphthapyrans (cf. VIII). In the solid state and in cold solutions these substances are colourless, but give deep blue solutions on warming (VII ⇌ VIII). Piperidinium salts are obtained when *spiro*dinaphthapyrans are dissolved in piperidine, the solutions being yellow whether cold or hot; (IX) is proposed for one of these piperidinium salts (Dilthey and Wizinger, *Ber.*, 1926, **59**, 1856).


(VI.)


(VII; Colourless.)


(VIII; Blue.)


(IX.)

A formula of type (IV) is the only one satisfactorily to explain all the foregoing phenomena.

EXPERIMENTAL.

Action of Piperidine on the Coloured Dimer (IV).—The dimer (1 g.) (Langenbeck and Langenbeck, *loc. cit.*) was dissolved in excess of piperidine (dried over potassium hydroxide) with the aid of gentle heat, and the red solution was left in a closed vessel for 3 days at room temperature; its colour faded gradually until it almost disappeared. Excess of piperidine was removed almost completely in a vacuum (bath temp. 80°), and the residue was mixed with petrol (b. p. 100—110°) (20 c.c.) and kept at room temperature. The colourless crystals (V) were filtered off and washed repeatedly with ligroin (b. p. 50—70°); m. p. 212° (decomp., giving a red melt). The *compound* is difficultly soluble in hot ligroin (b. p. 50—70°), hot benzene, or cold alcohol; but insoluble in water and cold dilute hydrochloric acid (Found: N, 5·0. $C_{38}H_{42}O_2N_2$ requires N, 5·0%).

Action of Heat on the Salt (V).—The salt (1 g.) was heated in a sealed evacuated vessel, fitted with a side tube ending in a small bulb, the latter being cooled in ice–salt. Heating was effected in a boiling ethyl cinnamate bath, and after 30 minutes the bulb, which contained a colourless liquid, was detached, and the liquid proved to be piperidine (picrate, from alcohol, m. p. 145° not depressed by admixture with an authentic sample; Rosenheim and Schidrowitz, *J.*, 1898, **73**, 144).

The deep violet solid which remained in the reaction vessel was dissolved in sufficient warm carbon tetrachloride; addition of alcohol (15 c.c.) precipitated some impurities, which were filtered off and the filtrate evaporated. The residue, crystallised from a small amount of ethyl acetate, proved to be (IV) (m. p. and mixed m. p. 168°; the substance gave an olive-green colour with concentrated sulphuric acid).

Irradiation of (IV).—The compound, partly dissolved and partly suspended in dry thiophen-free benzene, was exposed to sunlight (January to April) in a sealed Monax-glass tube filled with dry carbon dioxide, but was then recovered unchanged.

FOUAD I UNIVERSITY, ABBASSIA, CAIRO.

[*Received, January 2nd*, 1946.]