The structure, IV, was confirmed by elemental analysis, infrared spectral data NMR analysis,[6] and chemical behavior.

Because of the unpromising nature of the reaction by which IV was produced we have abandoned this line of attack.

EXPERIMENTAL[7]

2-Methyl-1,3-cyclopentanedione, I. This compound was prepared essentially as described.[3] However, on a scale which afforded 10–40 g. of pure I, m.p. 205–209° dec., we obtained yields in the 50–54% region or less when certain modifications were tried.[8]

2-Allyl-2-methyl-1,3-cyclopentanedione, II. Conditions for high yields of II on allylation of I were not found. In a typical experiment a mixture of 8.6 g. of I, 75 ml. of 1 *M* sodium hydroxide and 9.1 g. of allyl bromide was stirred at room temperature for 4 hr. Suitable treatment of the neutral fraction yielded 3.9 g. (34%) of II, b.p. 63–70° at 1 mm. and 4.3 g. (50%) of I was recovered from alkaline extracts of the reaction mixture. Redistillation of crude II afforded pure II, b.p. 61–62° at 1 mm., m.p. 6.0–6.5° (time-temperature cooling curve).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.0; H, 8.0. Found[g]: C, 71.3; H, 7.9.

The bis-2,4-dinitrophenylhydrazone[9] of II melted at 248–252° dec., and was formed in 76% yield.

Anal. Calcd. for $C_{21}H_{20}N_8O_8$: C, 49.2; H, 3.9; N, 21.9. Found[s]: C, 49.2; 49.2; H, 4.0, 4.1; N, 22.0, 22.1.

1-(2-Methoxy-6-naphthyl)-5-methyl-7-octene-1,4-dione, IV. To a solution of 15.2 g. of II in 100 ml. of ether at −10° was added an equivalent of titrated[4] 2-methoxy-6-naphthyllithium, the mixture was stirred at −10 to 0° for 1 hr., and then added slowly to 200 ml. of cold dilute hydrochloric acid. Steam distillation of 10 g. of the resulting dark oily product (29.5 g.) yielded 3 g. of 2-methoxynaphthalene and 1 g. of II. Chromatography of the residue on alumina yielded a total of 2.1 g. (7% based on starting II) of IV,[6] m.p. 78.4–78.8°, infrared absorption at 5.82, 5.94, 7.90, 9.72, 10.15, and 10.90 μ.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.4; H, 7.2. Found[g]: C, 77.7, 77.8; H, 7.3, 7.5.

A solution containing 0.033 mole of the Grignard reagent from 2-methoxy-6-bromonaphthalene in tetrahydrofuran was added to a solution of 5.0 g. of II in 25 ml. of tetrahydrofuran at 0°. After 15 min. a negative Gilman color test showed the absence of Grignard reagent. From the neutral portion of the products 4.3 g. (0.027 mole) of 2-methoxynaphthalene, m.p. 68–70°, not depressed by mixing with authentic 2-methoxynaphthalene, m.p. 71–72°. This indicates that II reacts in the Grignard reaction mainly by the enolization mechanism.[10]

1-(2-Methoxy-6-naphthyl)-5-methyl-1,4-octanedione, V. A solution of 0.37 g. of IV in alcohol was catalytically reduced over platinum until 1 equivalent of hydrogen had been absorbed (30 min.). By recrystallization from ether-petroleum ether (b.p. 30–60°) there was obtained 0.32 g. (86%) of V,[5] m.p. 87.0–88.0°. The infrared spectrum was almost identical to that of IV, except for the bands at 10.15 and 10.90 μ (terminal methylene) which were absent.

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.9; H, 7.7. Found[s]: C, 76.8; H, 7.8.

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(6) We are indebted to Dr. G. V. D. Tiers, Minnesota Mining and Manufacturing Company, Minneapolis, Minn., for the NMR analysis and interpretation thereof.

(7) Analyses marked g by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and s by Schwartzkopf Microanalytical Laboratories, Woodside 77, N. Y. All melting points are uncorrected.

(8) C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2022 (1959) report a 51% average yield in thispreparation.

(9) Prepared using Johnson's procedure. G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

(10) We are indebted to Mr. N. Venkateswaran for this experiment.

Reaction of Ivanov and Ivanov-Like Reagents with Iodine

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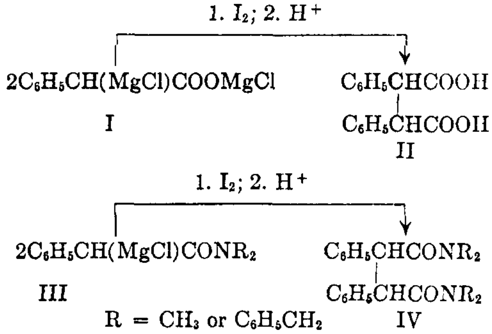
It has been found that the Ivanov reagent (I), prepared from phenylacetic acid, and the Ivanov-like reagents (III), obtained from *N,N*-dimethyl- and *N,N*-dibenzylphenylacetamide, respectively, reacted with iodine in the manner indicated below. The reaction products were *meso*-α,α'-diphenylsuccinic acid (II) (55% yield), *N,N,N',N'*-tetramethyl-(II), and *N,N,N',N'*-tetrabenzyl-α,α'-diphenylsuccindiamide (IV).



$$2C_6H_5CH(MgCl)COOMgCl \xrightarrow{1.\ I_2;\ 2.\ H^+} \begin{array}{l} C_6H_5CHCOOH \\ \quad | \\ C_6H_5CHCOOH \end{array}$$

I II

$$2C_6H_5CH(MgCl)CONR_2 \xrightarrow{1.\ I_2;\ 2.\ H^+} \begin{array}{l} C_6H_5CHCONR_2 \\ \quad | \\ C_6H_5CHCONR_2 \end{array}$$

III IV

$R = CH_3$ or $C_6H_5CH_2$

Ivanov and Spasov[1] found that sodium α-chloromagnesiumphenylacetate reacted with bromine to form *meso*-α,α'-diphenylsuccinic acid in 22% yield;. phenylbromoacetic acid was obtained as a byproduct. Recently, Panaiotov[2] treated the same Ivanov reagent with iodine and isolated *meso*-α,α'-diphenylsuccinic acid in 17% yield.

meso-α,α'-Diphenylsuccinic acid was treated with lithium aluminum hydride to produce 2,3-diphenyl-1,4-butanediol. It was expected that the diol might react with bromoacetal to form 2-bromomethyl-5,6-diphenyl-1,3-dioxalane. However, instead of this substance, a product was obtained in 39% yield which, based on analytical data, was 3,4-diphenyltetrahydrofuran.

EXPERIMENTAL

meso-α,α'-Diphenylsuccinic acid. Phenylacetic acid (136.1 g., 1.0 mole), dissolved in 500 ml. of benzene, was added,

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(1) D. Ivanov and A. Spassov, *Archiv hem. i. farm.*, **8**, 8 (1934); *Chem. Abstr.*, **28**, 6711 (1934).

dropwise, to a stirred solution of isopropylmagnesium chloride which had been prepared from 48.6 g. (2.0 g.-atoms) of magnesium, 157.1 g. of isopropyl chloride, 750 ml. of ether, and 4 ml. of ethyl bromide. The mixture was stirred and refluxed for 20 hr.

Iodine (126.9 g., 0.5 mole), dissolved in 1000 ml. of ether, was added, dropwise, to the stirred mixture. After the material had been stirred for 140 hr., it was poured into a mixture of 167 ml. of concd. hydrochloric acid, ice, and 1000 ml. of water and then stirred for an hour. The layers were separated, the aqueous layer was extracted with benzene, and the solvents were removed from the combined organic solutions in a stream of air. The crystalline material was filtered and exposed to air for several days to remove traces of iodine. The product, after recrystallization from acetic acid, weighed 75.0 g. (55%); m.p. 239–240°.[3]

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135.1. Found: C, 71.12; H, 5.52; neut. equiv., 135.8.

N,N,N′,N′-Tetramethyl-α,α′-diphenylsuccindiamide. N,N-Dimethylphenylacetamide[4] (32.6 g.), dissolved in 250 ml. of ether, was added, dropwise, to a stirred solution of isopropylmagnesium chloride prepared from 4.8 g. of magnesium, 16.5 g. of isopropyl chloride, 500 ml. of ether, and 4 ml. of ethyl bromide. Iodine (25.4 g.), dissolved in 250 ml. of ether, was added, dropwise, to the stirred mixture followed by the addition of 500 ml. of benzene. The material was stirred and refluxed for 3 hr. and then stirred for 20 hr. at room temperature. After the addition of a mixture of 16 ml. of concd. hydrochloric acid and 500 ml. of ice water, the layers were separated, and the solvents were removed from the organic layer in a stream of air. The brown residue became crystalline after trituration with acetone. The product, after recrystallization from ether, weighed 7.9 g. (24%); m.p. 193–194°.

Anal. Calcd. for $C_{20}H_{24}O_2N_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.02; H, 7.30; N, 8.46.

N,N-Dibenzylphenylacetamide. Dibenzylamine (197.3 g.) was dissolved in 1 l. of ether, the solution was stirred and 58.8 g. of phenylacetyl chloride[5] was added, dropwise. After the mixture had been stirred for 4 hr., the precipitated dibenzylamine hydrochloride was filtered. Removal of the solvent from the filtrate yielded 83.2 g. (69%) of product; m.p. 64–65° after recrystallization from ether.

Anal. Calcd. for $C_{22}H_{21}ON$: C, 83.77; H, 6.71. Found: C, 83.78; H, 6.66.

N,N,N′,N′-Tetrabenzyl-α,α′-diphenylsuccindiamide. This compound was obtained in 15% yield from N,N-dibenzylphenylacetamide by the process described above; m.p. 172–173° after recrystallization from ether.

Anal. Calcd. for $C_{44}H_{40}O_2N_2$: C, 84.04; H, 6.41. Found: C, 83.99; H, 6.19.

2,3-Diphenyl-1,4-butanediol. Lithium aluminum hydride (5.9 g.) was suspended in 750 ml. of ether, stirred and a suspension of 21.6 g. of *meso*-α,α′-diphenylsuccinic acid in 750 ml. of ether was added slowly. The mixture was stirred for 24 hr., cooled, stirred, and 12 ml. of water was added, dropwise. After filtration, the solvent was removed from the filtrate and the residue was recrystallized from benzene; yield 10.8 g. (55%); m.p. 143–144°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.27; H, 7.54.

Isolation of 3,4-diphenyltetrahydrofuran from the attempted preparation of 5,6-diphenyl-2-bromomethyl-1,3-dioxolane. A mixture of 9.7 g. (0.04 mole) of 2,3-diphenyl-1,4-butanediol, 7.9 g. (0.04 mole) of bromoacetal, 1 ml. of concd. hydrochloric acid and 1 ml. of concd. sulfuric acid was placed in a Claisen flask and heated in an oil bath. As the bath temperature was raised slowly from 95–150°, an unidentified liquid distilled. The residue was then distilled under reduced pressure; b.p. 142° (0.9 mm.). The distillate solidified rapidly and was recrystallized from ethanol; m.p. 86–88°; yield 3.5 g. (39%).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.67; H, 7.07.

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[2] I. M. Panaiotov, *Compt. rend. acad. bulgare sci.*, **9**, No. 3, 25 (1956); *Chem. Abstr.*, **52**, 1974 (1958).

[3] I. A. Smith [*Ber.*, **71**, 641 (1938)], m.p. 242–243°.

[4] H. J. Taverne, *Rec. trav. chim.*, **16**, 37 (1897).

[5] P. Truitt, D. Mark, L. M. Long, and J. Jeanes, *J. Am. Chem. Soc.*, **70**, 4214 (1948).

Structure of Phthalocyanine[1]

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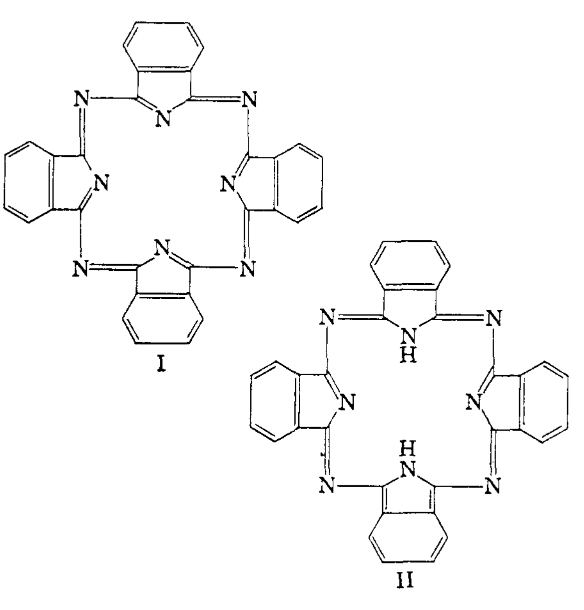
Of the two suggested formulas for phthalocyanine $(C_8H_4N_2)_4$ (I) or $(C_8H_4N_2)_4H_2$ (II) various lines of evidence have shown II to be the most probable.[2] Nevertheless, the analytical difference has been too small to be resolved by conventional combustion techniques, and a direct demonstration of Formula II is lacking.



I

II

In developing syntheses of deuterio-phthalocyanine we have obtained analyses which show that $^2/_{18}$ of the total hydrogens are easily replaced by deuterium under conditions such that copper phthalocyanine shows no exchange. This is taken to indicate that there are 18 hydrogen atoms per mole and that two of them differ chemically from the others in accord with formula II.

An infrared peak at 3298 cm.$^{-1}$ has been reported for phthalocyanine and attributed to two

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, **1934**, 1031; C. E. Dent, R. P. Linstead, and A. R. Lowe, *J. Chem. Soc.*, (1033).