TABLE I

BIS-DIALKYLAMINOALKYL 5-METHOXYISOPHTHALATE DIHYDROCHLORIDES

Bis-dialkylaminoalkyl 5-methoxyisophthalate dihydrochloride	Yield, %	M. p., °C.	Formula	Nitrogen, % Calcd.	Found
β-(Dimethylamino)-ethyl	46.0	224–225	$C_{17}H_{28}O_5N_2Cl_2$	6.81	6.71
β-(Diethylamino)-ethyl	59.5	227	$C_{21}H_{36}O_5N_2Cl_2$	5.99	6.07
γ-(Diethylamino)-propyl	72.5	178–179	$C_{23}H_{42}O_5N_2Cl_2$	5.65	5.64
β-(Di-n-propylamino)-ethyl	50.0	151–152	$C_{25}H_{44}O_5N_2Cl_2$	5.35	5.28
γ-(Di-*n*-propylamino)-propyl	65.8	139–140	$C_{27}H_{48}O_5N_2Cl_2$	5.07	4.94
β-(Di-isopropylamino)-ethyl	52.0	188–189	$C_{25}H_{44}O_5N_2Cl_2$	5.35	5.23
γ-(Di-isopropylamino)-propyl	63.8	119	$C_{27}H_{48}O_5N_2Cl_2$	5.07	5.00
β-(Di-*n*-butylamino)-ethyl	69.1	137.5–138.5	$C_{29}H_{52}O_5N_2Cl_2$	4.83	4.74
γ-(Di-*n*-butylamino)-propyl	63.5	127–128	$C_{31}H_{56}O_5N_2Cl_2$	4.59	4.50
β-(Di-*n*-amylamino)-ethyl-[a]	65.2	.....	$C_{33}H_{58}O_5$	4.96	4.78
γ-(Di-*n*-amylamino)-propyl	35.8	70–72	$C_{35}H_{64}O_5N_2Cl_2$	4.22	4.22
β-(Di-*n*-hexylamino)-ethyl[b]	62.1	64–65	$C_{37}H_{66}O_5N_2Br_2$	3.59	3.63
γ-(Di-*n*-hexylamino)-propyl	77.5	75–76	$C_{39}H_{74}O_5N_2Cl_2$	3.89	3.96

[a] Free base b. p. 205–210° (0.05 mm.). [b] Dihydrobromide.

CHEMISTRY DEPARTMENT
NORTHWESTERN UNIVERSITY DENTAL SCHOOL
CHICAGO 11, ILLINOIS RECEIVED[6] AUGUST 17, 1949

(6) Original manuscript received July 16, 1947.

The Formation of Biphenyl in the Decomposition of Benzoyl Peroxide in Nitrobenzene

BY DELOS F. DETAR

In the decomposition of diacyl peroxides $(ArCOO)_2$ in aromatic solvents it has been observed[1] that the principal product is the unsymmetrical biaryl ArAr[1] formed by attack on the solvent. In the decomposition of benzoyl peroxide in nitrobenzene Wieland, Schapiro and Metzger[2] were unable to detect any of the symmetrical product, biphenyl. With the idea that more biphenyl might be formed in more concentrated solutions, the experiment[2] was repeated with 20–40% solutions. Biphenyl was definitely formed and probably in at least 3–4% yields since the isolation method is known to involve losses. The biphenyl may have been formed by either a coupling of two phenyl radicals, or by an induced decomposition of the peroxide by a phenyl radical.[3,4] No more than a trace of the symmetrical 4,4′-dinitrobiphenyl could have been present since none could be found. It is much less soluble than the 4-nitrobiphenyl and is detectable in mixtures with it.

Experimental

Decomposition of Benzoyl Peroxide in Nitrobenzene.—Benzoyl peroxide (5.00 g.) was added to 15 g. of nitrobenzene and the mixture warmed at 110° for one-half hour (homogeneous solution). The reaction mixture was steam distilled, the distillate extracted with alkali and then the nitrobenzene layer was reduced with tin and hydrochloric acid.[5] Steam distillation of the reduction mixture followed by extraction with peroxide-free ether gave a neutral residue. This was refluxed with 10% sodium hydroxide solution to assure removal of phenyl benzoate. The residue amounted to 44 mg. (1.4%). It was identified as biphenyl by microscopic comparison with authentic biphenyl by identity of the 70° angle of the rhombic-shaped plates obtained from ethanol and the extinction angles which bisected the vertices. Other runs at 90° and one decomposition of a 40% solution of benzoyl peroxide gave similar results.

(1) *Cf.* Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1946, p. 165.
(2) Wieland, Schapiro and Metzger, *Ann.*, **513**, 105 (1934).
(3) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).
(4) DeTar and Sagmanli, *ibid.*, **72**, 965 (1950).
(5) This reduction method was used by Wieland, Schapiro and Metzger.[2]

THE BAKER LABORATORY OF CHEMISTRY
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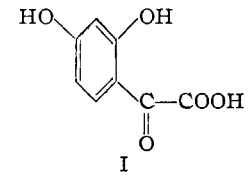
ITHACA, NEW YORK RECEIVED AUGUST 26, 1949

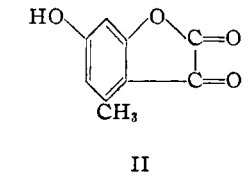
The Ultraviolet Absorption Spectra of Several Substituted Phenylglyoxylic Acids

BY DONALD J. CRAM

In connection with a study on the structure of citrinin, the compounds I,[1] II,[1] III[1] and IV[1] were synthesized as models for an ultraviolet absorption spectra comparison with citrinin. Although the recent resynthesis of this natural product[2] made such a study unfeasible, an examination of the spectra of these molecules reveals some interesting structural relationships.



I



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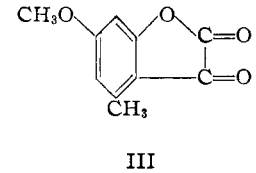
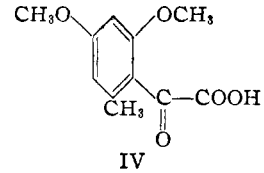


III



IV

Hunsberger, *et al.*,[1] reported that methylation of II with dry diazomethane produced a monomethylated compound that possessed the hemiquinone

(1) Hunsberger and Amstutz, THIS JOURNAL, **70**, 671 (1948).
(2) Robertson, *et al.*, *Nature*, **163**, 94 (1949).

TABLE I

ULTRAVIOLET ABSORPTION DATA[a]

Solvent	Compound I λmax., mμ	I log ε	II λmax., mμ	II log ε	III λmax., mμ	III log ε	IV λmax., mμ	IV log ε
Cyclohexane	...[b]	...	245	3.860	244	3.820	256	3.830
	...	...	312	3.993	309	3.899	281	3.878
							306	3.891
50% alc.	292	4.083	291	4.071	291	4.070	287	4.000
0.1 *N* HCl	310[c]	3.995	313[c]	3.95	315[c]	3.94	316	3.894
0.01 *N* NaOH	246[c]	3.88	245[c]	3.92	239	4.177	231[c]	3.96
	333	4.366	334	4.311	283	3.911	283	3.971
					365	3.829	307	3.860

[a] Beckman quartz spectrophotometer. [b] The low solubility of the substance in cyclohexane prevented the spectrum from being taken. [c] = point of inflection.

structure III'.[3] This same substance was obtained in the present investigation as one product of the methylation of II with dimethyl sulfate (IV was the other product).

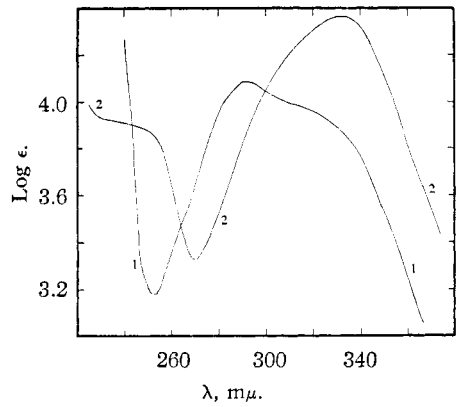


Fig. 1.—Ultraviolet absorption spectra of compound I (Beckman quartz spectrophotometer): curve 1, in 50% ethanol–50% 0.10 *N* hydrochloric acid; curve 2, in 0.01 *N* sodium hydroxide.

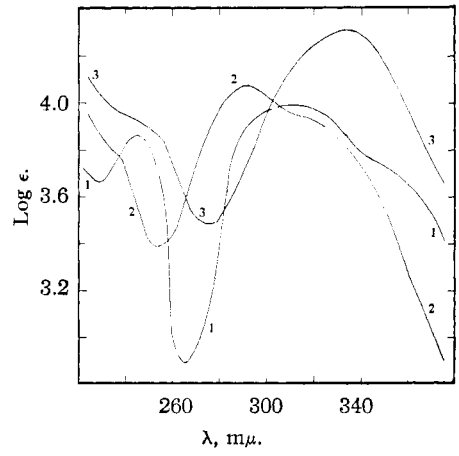
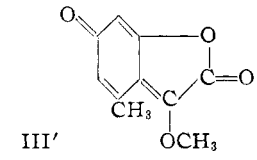


Fig. 2.—Ultraviolet absorption spectra of compound II (Beckman quartz spectrophotometer): curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 *N* hydrochloric acid; curve 3, in 0.01 *N* sodium hydroxide.

(3) The author is indebted to Drs. Hunsberger and Amstutz for a sample of the substance.



III'

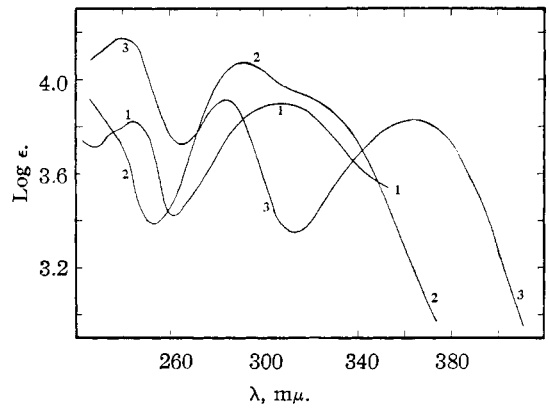


Fig. 3.—Ultraviolet absorption spectra of compound III (Beckman quartz spectrophotometer): curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 *N* hydrochloric acid; curve 3, in 0.01 *N* sodium hydroxide.

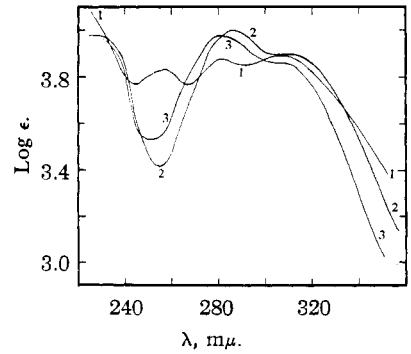


Fig. 4.—Ultraviolet absorption spectra of compound IV (Beckman quartz spectrophotometer): curve 1, in cyclohexane; curve 2, in 50% ethanol–50% 0.10 *N* hydrochloric acid; curve 3, in 0.01 *N* sodium hydroxide.

The spectra of II and III in cyclohexane suggest that the monomethylated substance possesses the benzenoid structure III rather than the hemiquinone structure III′. The similarity of all of the spectra in aqueous acid solution would indicate the rupture of the lactone ring in such media. In alkaline solution where phenolate and carboxylate ions are the absorbing chromophores the data suggest that I and II exist as *p*-phenolate–carboxylate ions and III as an *o*-phenolate–carboxylate ion. The slight difference between cyclohexane and aqueous acid solutions of IV can be attributed to solvent–solute hydrogen bonding in the latter medium.

Experimental

Preparation of I, II, III and IV.—The compounds 2,4-dihydroxyphenylglyoxylic acid (I) and 2,4-dihydroxy-6-methylphenylglyoxylic acid lactone (II) were prepared by the procedures of Hunsberger, *et al.*,[1] and melted at 167–168° and 216–217°, respectively. The latter substance was methylated in the following manner.

A mixture of 1.0 g. of II and 5 ml. of methanol was prepared and 5 g. of dimethyl sulfate and a solution of 30% potassium hydroxide in water added intermittently in small portions, keeping the mixture near the neutral point. When the addition was complete (the mixture was slightly basic), water was added and the white needles that separated were recrystallized from ethanol and water to give 0.23 g. of the methyl ester of IV, m. p. 73–74°, which upon saponification gave 0.19 g. of IV, m. p. 139–141°,[1] (colorless needles from ethanol and water).

The filtrates from the crystallization of the ester were acidified and the yellow needles that separated were collected and recrystallized from ethanol and water to give 0.18 g. of III (yellow needles) m. p. 169–171°, m. m. p. with the monomethylated lactone prepared by Hunsberger,[1] 168–170°.

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Di-*n*-propylnitramide and its Isomer

BY W. R. KINGDON AND GEORGE F WRIGHT

Considerable confusion exists with respect to the compounds known as isonitramines. This is owing, firstly, to the fact that the addition products of nitric oxide with active methylenic compounds have been called isonitramine salts[1] although they are generally considered to be the salts of nitrosohydroxylamines.[2]

Secondly, such an error in nomenclature is not unexpected in view of the fact that the isonitramine structure, II, is not known with certainty but only as isomeric with the unequivocal secondary nitramide structure I, together with which it is formed when a primary nitramide salt is treated with an alkyl iodide (M is silver or potassium).

Thirdly, the confusion will not be diminished by the recent revision in nomenclature whereby I, formerly known as di-*n*-propylnitramine, is now to be classified for index purposes as di-*n*-propylnitramide. Henceforth in the present paper the older terminology will be used, since comparison must be made with the isonitramines, for which there seems at this writing to be no justification for change in nomenclature.

When both I and II are formed in the alkylation reaction, the isonitramine may be recognized by its lower boiling point and its lesser stability toward acid and alkali. Sometimes both isomers are not produced. This was the case when Thomas[3] treated silver *n*-propylnitramine with *n*-propyl iodide. He designated his single product as di-*n*-propylnitramine (b. p. 76–79° at 10 mm.). His formulation was supported by the observation[4] that the compound was stable toward hot dilute aqueous potassium hydroxide.

Secondary nitramines with saturated alkyl groups can now be prepared by direct nitration of the secondary amine.[5] When di-*n*-propylamine was nitrated in this manner the authentic di-*n*-propylnitramine was found to boil higher (103–104° at 10 mm.) than the compound reported by Thomas. Unlike Thomas' compound it melted sharply at 1.0–1.6° when it was separated entirely from di-*n*-propylacetamide and di-*n*-propylnitrosamine which were also produced by the nitration procedure.

For purposes of comparison Thomas' procedure was repeated to yield mainly the compound he reported, although a small amount (3% of theoretical) of the product of direct nitration was evidently obtained as well. This higher boiling fraction, unlike Thomas' compound, froze at a temperature below 0° and gave a positive Franchimont test for the nitramino linkage.[6] No isonitramine gives this test.

When the two compounds were heated with 5% aqueous potassium hydroxide neither decomposed appreciably, but Thomas' compound decomposed strongly with gas evolution when it was added to 70% sulfuric acid at 25°, while the product of direct nitration was quite stable toward this medium. We believe this acid test to be a better criterion for differentiation of nitramine and isonitramine than the alkali test. On this basis Thomas' compound must be the isonitramine.

Experimental[7]

***n*-Propyldichloramine** was prepared in 71% yield ($n^{24}D$ 1.4525, 98% electropositive chlorine) by passage of chlorine over eight hours into a solution of 33 g. (0.56 mole) of *n*-propylamine and 126 g. (1.5 moles) of sodium bicarbonate in 1 liter of water at 5–10°. The oil which settled out was washed successively with 5% aqueous sulfuric acid, 50% aqueous sulfuric acid and four times with water.

***n*-Propylnitramine** was prepared by simultaneous and equivalent addition of 51 g. (0.4 mole) of undistilled propyldichloramine and 76 g. (1.2 moles) of 99.3% nitric acid into 204 g. (2 moles) of stirred acetic anhydride at 7–32° over fifty minutes. The addition of acid was maintained 5% ahead of the dichloramine addition. After one hour of subsequent stirring the whole was poured into a

(1) W. Traube, *Ber.*, **27**, 1504 (1894).

(2) G. W. MacDonald and O. Masson, *J. Chem. Soc.*, **65**, 944 (1894).

(3) J. C. A. S. Thomas, *Rec. trav. chim.*, **9**, 69 (1890).

(4) H. van Erp, *Rec. trav. chim.*, **14**, 1 (1895).

(5) W. J. Chute, *et al.*, *Can. J. Research*, **26B**, 114 (1948).

(6) A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 226 (1897).

(7) All melting points are corrected against known standards.