hence

$$K_1 = 4\alpha_1^2c/(1 - \alpha_1) = 1.39 \times 10^{-2}$$
$$K_2 = 4\alpha_2^2c/(1 - \alpha_2) = 0.655 \times 10^{-2}$$

and solving equations 1, 2, 3, 4 and 5 above for (R_1)

$$(R_1) = \frac{K_1(K_2 + 4\alpha c) - \sqrt{K_1K_2(K_1 + 4\alpha c)(K_2 + 4\alpha c)}}{2(K_1 - K_2)}$$
$$(R_1) = 1.63 \times 10^{-2}M$$

from equation 4

$$(R_2) = 2\alpha c - (R_1)$$
$$(R_2) = 1.17 \times 10^{-2}M$$

then (equation 1)

$$(E_{11}) = (R_1)^2/K_1 = 1.91 \times 10^{-2}M$$

and from equation 5

$$(E_{12}) = c - 2(E_{11}) - (R_1)$$
$$(E_{12}) = 4.60 \times 10^{-2}M$$

therefore (equation 6)

$$K_{12} = 0.415 \times 10^{-2}$$

Equilibrium constants calculated in a similar manner for the "mixed ethanes" for which the apparent dissociation has been measured (1) are listed in Table I.

TABLE I

EQUILIBRIUM CONSTANTS FOR "MIXED ETHANES"

Chlorides used	$K_1 \times 10^2$	$K_2 \times 10^2$	$K_{12} \times 10^2$
o-Chlorophenyldiphenylmethyl		0.655	0.415
o-Bromophenyldiphenylmethyl	1.39		
o-Tolyldiphenylmethyl		3.33	1.82
α-Naphthyldiphenylmethyl	3.99		
o-Tolyldiphenylmethyl		3.33	1.03
Di-*o*-tolylphenylmethyl	149.0		
Tri-*p*-biphenylmethyl		3.33	1.67
Tri-β-naphthylmethyl	3.33		
p-*t*-Amylphenyldiphenylmethyl		0.278	0.0138
Phenyldi-*p*-*t*-amylphenylmethyl	0.356		
Tri-*p*-*t*-butylphenylmethyl	2,00		.0118
p-*t*-Butylphenyldiphenylmethyl		.243	

Since K_{12} is, in all cases, smaller than either K_1 or K_2, it is evident that the "mixed ethanes" have a greater free energy of dissociation than either of the parent ethanes.

There appears to be no simple mathematical relation between K_1, K_2 and K_{12}. It is probable that the value of K_{12} depends not only upon K_1 and K_2, but also upon such factors as polarization of the ethane bond, steric hindrance and the effect of symmetry upon the entropy of dissociation.[2]

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[2] Symmetry effects on the entropy of dissociation have been outlined in a private communication from Professor P. D. Bartlett.

2'-Hydroxydiphenylphthalide

BY MAX H. HUBACHER

We have discovered that interaction of 2-benzoylbenzoyl chloride with phenol yields not only 4'-hydroxydiphenylphthalide, isolated previously from this reaction by Blicke and Swisher,[1] but also the hitherto unknown, isomeric 2'-hydroxydiphenylphthalide (I).

In conformity with its structure, we find that Compound I can be converted into a monoacetyl derivative, and a monomethyl ether; the melting point of the latter corresponds to that of 2'-methoxydiphenylphthalide which has been obtained by other investigators[2] by an entirely different procedure.

Compound I does not react with hydroxylamine; when fused with potassium hydroxide, it is converted into 9-phenylxanthene.

Experimental Part[3]

2'-Hydroxydiphenylphthalide (I).—The acid chloride, made from 45.2 g. (0.20 mole) of 2-benzoylbenzoic acid and 26 g. (0.22 mole) of thionyl chloride, was warmed for two hours at 40° with a solution of 18.8 g. (0.20 mole) of phenol in 300 ml. of benzene.[1] The crude 4'-hydroxydiphenylphthalide produced was recrystallized from acetic acid: 46 g. melting at 151-155° was obtained. All of this material, in 2-g. portions, was placed in a sublimation apparatus fitted with a water-cooled condenser,[4] and kept at 150° under 10 microns pressure. The total sublimate (m. p. 160-210°), after several recrystallizations from acetic acid, weighed 2.1 g., and melted at 240.5-241.3°. This compound, 2'-hydroxydiphenylphthalide (I), dissolved completely in 2.5 *N* sodium hydroxide to form a colorless solution. Its solution in concentrated sulfuric acid was orange.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 5.00; mol. wt., 302. Found: C, 79.20, 79.35; H, 5.30, 4.43; mol. wt., 282 ± 12 (Rast, in camphor).

The portion of the 4'-hydroxydiphenylphthalide (m. p. 151-155°) which had not been sublimed, was recrystallized several times from acetic acid, whereupon pure 4'-hydroxydiphenylphthalide (m. p. 170.1-170.4°) (1) was obtained.

The acetyl derivative of 2'-hydroxydiphenylphthalide was formed when 0.608 g. of it, 3 ml. of acetic acid, 1 ml. of acetic anhydride and a drop of concentrated sulfuric acid were refluxed for one hour. It melted at 136.6-137.7° after recrystallization from ethanol (1 g. in 10 ml.).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.70. Found: C, 76.44; H, 4.52.

2'-Methoxydiphenylphthalide was obtained when I was

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[1] F. F. Blicke and R. D. Swisher, THIS JOURNAL, **56**, 924 (1934), report a m. p. of 168-170° for the 4'-hydroxydiphenylphthalide.

[2] F. F. Blicke and O. J. Weinkauff, *ibid.*, **54**, 1452 (1932), reported this compound as melting at 127-128°.

[3] All melting points are corrected.

[4] This apparatus is described in *J. Ind. Eng. Chem., Anal. Ed.*, **15**, 448 (1943).

methylated with dimethyl sulfate. After several recrystallizations from ethanol, it melted at 126.1–126.7°.[2] A mixed melting point (about 100°) proved that this substance was not identical with the isomeric 2-(4′-methoxybenzoyl)-benzophenone,[5] which melts at 135.8–136.7°.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.10; —OCH_3, 9.81. Found: C, 79.53; H, 4.59; —OCH_3, 9.54.

One-half gram of the 2′-hydroxydiphenylphthalide and 5 g. of potassium hydroxide were placed in a nickel crucible, and the latter immersed for five minutes in an oil-bath which was maintained at 240–245°. The reaction products were a small amount of benzoic acid and a substance insoluble in cold 2.5 *N* sodium hydroxide or concentrated sulfuric acid. The latter compound, which proved to be 9-phenylxanthene, was purified by sublimation at 140° under 10 microns pressure,[4] followed by two crystallizations from ethanol; yield 50 mg.; m. p. 145.1–145.5°.[6]

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 87.90; H, 5.20.

Mixed with a sample of 9-phenylxanthene, prepared according to the method of Ullmann and Engi, the material melted at 145.0–145.7°.

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(5) Ref. 1, page 923. A sample of this benzophenone was obtained through the courtesy of Professor Blicke.

(6) F. Ullmann and G. Engi (*Ber.*, **37**, 2372 (1904)) found 145°.

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Note on the Geometrical Isomerism of Cyclic Acetals Derivable from Nitro Polyhydric Alcohols

BY MURRAY SENKUS

An inspection of the structure of 1,3-dioxanes in which carbon atoms 2 and 5 carry two different atoms or groups reveals that these heterocyclic compounds are capable of existing in two geometrically isomeric forms. Hibbert and Carter recognized this fact during their study of the cyclic acetals of glycerol and demonstrated geometrical isomerism of this heterogeneous ring for the first time when they isolated two geometrical modifications of 5-methoxy-2-*p*-nitrophenyl-1,3-dioxane, 5-benzoyl-2-*p*-nitrophenyl-1,3-dioxane, and 5-*p*-nitrobenzoyl-2-*p*-nitrophenyl-1,3-dioxane.[1]

It has been reported from this Laboratory that nitro polyhydric alcohols derivable from normal nitroparaffins and formaldehyde react with aldehydes in the presence of *p*-toluenesulfonic acid to give substituted 5-nitro-1,3-dioxanes in conversions which average about 90%; also that hydrogenation of these nitro acetals yields the corresponding amino acetals.[2] All of these dioxanes in which carbon atoms 2 and 5 carry two different atoms or groups should exhibit geometrical isomerism. Reference to these isomers was omitted from my original paper but since it has been suggested that further information on this general subject would be of interest, the following information regarding the isolation of two isomeric forms of two dioxanes is being submitted.

Experimental

Isomeric Benzaldehyde Acetals of 2-Nitro-2-methyl-1,3-propanediol.—Six hundred milliliters of cyclohexane and 160 ml. of benzene were added to the crude dry product obtained from the reaction of 1 mole of benzaldehyde with 1 mole of 2-nitro-2-methyl-1,3-propanediol. The mixture was agitated at 15° for fifteen minutes and filtered. The dried solid (180 g.) melted at 116.8°. This isomer when purified by recrystallization from methanol melts at 118.3°.[2]

The filtrate from the initial filtration was distilled until 400 ml. of distillate had been obtained. The residue was cooled to 15° for fifteen minutes, during which time a second crop of crystals was obtained. The solid was filtered and dried overnight at room temperature. The product melted at 73.7° and weighed 26 g. The filtrate from the residue filtration was concentrated further and 7 additional grams of product obtained, m. p. 77.5°. The two crops of crystals were combined and purified by recrystallizing twice from butyl ether. The pure isomer melted at 78.4°.

Anal. Calcd. for $C_{11}H_{13}O_4N$: N, 6.28. Found: N, 6.32.

This isomer was hydrogenated in 95% conversion to the corresponding amino acetal according to the reported method.[2] It was purified by recrystallization from cyclohexane; m. p. 48.2°. The other amino isomer which had been prepared previously melts at 84.0°.

Anal. Calcd. for $C_{11}H_{15}O_2N$: N, 7.25. Found: N, 7.30.

Isomeric Butyraldehyde Acetals of 2-Nitro-2-ethyl-1,3-propanediol.—Eleven hundred grams of 2-nitro-2-ethyl-1,3-propanediol (7.38 moles) was allowed to react with 550 g. of butyraldehyde (7.64 moles) according to the reported procedure.[2] The product was rectified through a one-foot Vigreux column at a 5:1 reflux ratio. The lower-boiling isomer (178 g.) distilled at 104–106° at 5 mm.

Anal. Calcd. for $C_9H_{17}O_4N$: N, 6.90. Found: N, 7.11; n^{20}_{D} 1.4501; d^{20}_{20} 1.0882.

The higher-boiling isomer (1193 g.) distilled at 136.0–136.5° at 5 mm.

Anal. Calcd. for $C_9H_{17}O_4N$: N, 6.90. Found: N, 7.04; n^{20}_{D} 1.4550; d^{20}_{20} 1.1052.

The amino acetal prepared from the low-boiling isomer distilled at 94–95° at 10 mm.; conversion, 95%.

Anal. Calcd. for $C_9H_{19}O_2N$: N, 8.09. Found: N, 8.12; n^{20}_{D} 1.4531; d^{20}_{20} 0.9740.

The amino acetal prepared from the high-boiling isomer distilled at 95° at 10 mm.; conversion, 95%.

Anal. Calcd. for $C_9H_{19}O_2N$: N, 8.09. Found: N, 7.93; n^{20}_{D} 1.4479; d^{20}_{20} 0.9676.

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(1) Hibbert and Carter, THIS JOURNAL, **50**, 3376 (1928).

(2) Murray Senkus, *ibid.*, **63**, 2635 (1941).