

thiocyanate ion must be more or less dissociated in solution, and we do not wish to deny that ions of the type postulated by Møller and by Bent and French play an important role in this test.

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Dicyclopentadiene: Preparation from the Monomer; Dielectric Constants of Dimer at Several Temperatures

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The usual method of preparing dicyclopentadiene is to fractionally distill the crude, impure dimer, and allow it to polymerize at room temperature overnight. This procedure is repeated a number of times, depending upon the purity of the original material, until a fraction is obtained that distills over at 41.5°—the boiling point of pure cyclopentadiene. When this latter material polymerizes, it yields a white, crystalline solid. The accepted values for the melting point and refractive index of dicyclopentadiene are given as 31.5° and 1.5120 (20°), respectively.

In an attempt to shorten the preparation of the dimer, we have adopted a slightly different procedure. Dicyclopentadiene obtained through the courtesy of the Research Laboratory of the United Gas Improvement Co. of Philadelphia was a faint straw-colored liquid containing 98% dimer. It was fractionally distilled once, and the distillate which came over between 40 and 44° was collected. This was allowed to stand overnight at 15°. The incompletely polymerized liquid was then placed under vacuum to remove the last traces of monomer and any other volatile impurities. Crystallization took place suddenly. The melting point of this crystalline solid was 27.8°, corrected, but the refractive index of the melt was identical with that of the solid which melted at 31.5°. After resolidification, the melting point was 31.5°, the same as that of the dicyclopentadiene prepared by the previous method.

It was found that low temperature (15–20°) was essential to the formation of the above crystals which we shall call an isomer of dicyclopentadiene. This form of the dimer was readily reproducible, the melting point being 27.8° for each preparation. The melting point and freezing point after resolidification was always 31.5°. When polymerization was carried out at slightly

higher temperatures and when polymerization was not hastened by pumping off the more volatile monomer, the solid produced melted at 31.5° and possessed a strong, camphor-like odor. The isomer, on the other hand, had only a slight odor. Microscopic examination showed the crystalline forms to be quite different.

This evidence seems to indicate that a polymorph or an isomer of dicyclopentadiene has been obtained. From the accepted formula of this compound, *cis* and *trans* isomers are possible. It is reasonable to assume that these two forms exist as dynamic isomerides, since any operation which changes the form of the crystals melting at 27.8° leads, upon resolidification, to the more stable form having a melting and freezing point of 31.5°.

Experimental.—The dielectric constants were measured with a parallel resistance bridge previously described.¹ The beat frequency was set at 1000 cycles. A small multiple plate variable condenser inserted in a small Pyrex tube was used as the cell. About 25 ml. of liquid sample was required to completely immerse the plates of the condenser. The cell assembly was placed in a thermoregulated oven which was controlled to $\pm 0.05^\circ$. The capacitance of the cell in air did not change over the temperature range employed. The time allowed for the temperature of the cell to reach equilibrium with the oven was forty-five minutes for each 10°.

No difference in dielectric measurements was observed when a frequency of 21,000 cycles was used instead of 1000. The values of the dielectric constant of dicyclopentadiene thus obtained were

$t^\circ \text{C.}$	40	50	60	70	80	90	100
ϵ	2.43	2.41	2.39	2.37	2.35	2.33	2.31

These data indicate that over this temperature range dicyclopentadiene does not possess a very high dipole moment.

(1) American Society for Testing Materials, Specification D150 36T.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
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NEW COMPOUNDS

Phenacyl, *p*-Phenyl- and *p*-Bromophenacyl, and *p*-Nitrobenzyl Esters of Certain α -Hydroxy Fatty Acids

The authors recently had occasion to synthesize a series of α -hydroxy fatty acids, of which, among other derivatives, the following new esters were prepared. The procedures for their preparation and for the determination of

Acid	Ester	M. p. (cor.) °C.	Empirical formula	Analyses, % ^a			
				Calcd.		Found	
			C	H	C	H	
α -Hydroxy-caprylic	Phenacyl	55.5-56.5	C ₁₈ H ₂₂ O ₄	69.02	7.97	68.92	8.07
	<i>p</i> -Phenylphenacyl	88.0-89.7	C ₂₂ H ₂₆ O ₄	74.53	7.40	74.57	7.35
	<i>p</i> -Bromophenacyl	95.0-95.8	C ₁₉ H ₂₁ BrO ₄	53.81	5.93	54.02	5.81
α -Hydroxy-capric	<i>p</i> -Nitrobenzyl	Oil					
	Phenacyl	60.0-60.5	C ₁₈ H ₂₆ O ₄	70.54	8.54	70.29	8.42
	<i>p</i> -Phenylphenacyl	80.3-80.8	C ₂₂ H ₃₀ O ₄	75.35	7.91	75.32	8.01
	<i>p</i> -Bromophenacyl	93.0-93.5	C ₁₉ H ₂₅ BrO ₄	56.09	6.54	55.86	6.54
α -Hydroxy-lauric ^a	<i>p</i> -Nitrobenzyl	54.5-55.5	C ₁₇ H ₂₅ NO ₅	63.12	7.80	63.16	7.63
	Phenacyl	63.5-64.0	C ₂₀ H ₃₀ O ₄	71.81	9.05	71.80	9.06
	<i>p</i> -Bromophenacyl	91.0-91.5	C ₂₀ H ₂₉ BrO ₄	58.09	7.08	57.83	7.03
α -Hydroxy-myristic	<i>p</i> -Nitrobenzyl	59.0-59.5	C ₁₉ H ₂₉ NO ₅	64.91	8.32	64.94	8.36
	Phenacyl	69.0-69.5	C ₂₂ H ₃₄ O ₄	72.87	9.46	72.47	9.40
	<i>p</i> -Bromophenacyl	95.0-95.4	C ₂₂ H ₃₃ BrO ₄	59.84	7.54	59.72	7.40
α -Hydroxy-palmitic	<i>p</i> -Nitrobenzyl	67.0-68.0	C ₂₁ H ₃₃ NO ₅	66.45	8.77	66.32	8.99
	Phenacyl	69.8-70.1	C ₂₄ H ₃₆ O ₄	73.79	9.81	73.68	9.86
	<i>p</i> -Bromophenacyl	96.0-96.5	C ₂₄ H ₃₇ BrO ₄	61.38	7.95	61.78	7.86
α -Hydroxy-stearic	<i>p</i> -Nitrobenzyl	69.5-70.5	C ₂₃ H ₃₇ NO ₅	67.76	9.16	67.78	9.14
	Phenacyl	76.4-76.8	C ₂₆ H ₄₂ O ₄	74.58	10.12	74.25	10.00
	<i>p</i> -Bromophenacyl	98.0-98.5	C ₂₆ H ₄₁ BrO ₄	62.74	8.31	62.52	8.25
	<i>p</i> -Nitrobenzyl	76.5-77.0	C ₂₈ H ₄₁ NO ₅	68.91	9.49	69.20	9.32

^a The *p*-phenylphenacyl esters α -hydroxy-lauric, myristic, palmitic and stearic acids separated from aqueous alcohol as gelatinous masses. Repeated attempts to purify them for analysis met with failure.

their melting points are described in a previous communication.¹

(1) Price and Griffith, THIS JOURNAL, 62, 2884 (1940).

(2) Microanalyses carried out by Dr. Everette L. May of this Laboratory.

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DONALD PRICE
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α -Naphthylcyclohexanol-1

To an ethereal solution of α -naphthylmagnesium bromide prepared from 50 g. of α -bromonaphthalene and 6.5 g. of magnesium were added, after one hour, 100 ml. of benzene and then during a fifteen minute period 25 g. of cyclohexanone dropwise with stirring. The alcohol was isolated in the usual way. The oil so obtained crystallized after several weeks. The crystals were washed with cold petroleum ether and then recrystallized three times from the same solvent. The substance formed transparent, colorless rhomboids; m. p. 66-68°, yield 40%.

Anal. Calcd. for C₁₆H₁₈O: C, 85.00; H, 7.96. Found: C, 85.14; H, 7.95.

The preparation of this substance was previously reported in the literature,¹ but it was not purified and no quantitative data regarding it were given.

(1) Sherwood, Short and Stansfield, *J. Chem. Soc.*, 1834 (1932).

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Some Chlorophenoxyacetic Acids

2,4-Dichlorophenoxyacetic Acid.—Equimolecular quantities of 2,4-dichlorophenol (5.0 g.) and monochloroacetic acid (2.9 g.) were heated with a slight excess (2.7 g.) of sodium hydroxide, and 15 cc. of water, until the solution was evaporated almost to dryness. The residue was then dissolved in 100 cc. of hot water, the solution cooled to room temperature and acidified with hydrochloric acid. A heavy oil separated which soon crystallized. The mixture was extracted with ether, the ether extract washed with water and evaporated to dryness on the water-bath. The yield of 2,4-dichlorophenoxyacetic acid was 5.9 g. (87%); recrystallized from benzene, m. p. 138°; white odorless crystals, almost insoluble in water.

Anal. Calcd. for C₈H₆O₂Cl₂: Cl, 32.08; neut. equiv., 221.0. Found: Cl, 32.10; neut. equiv., 221.

2,4,5-Trichlorophenoxyacetic Acid.—Equimolecular quantities of 2,4,5-trichlorophenol (5.0 g.) and monochloroacetic acid (2.4 g.) were heated with a slight excess (2.2 g.) of sodium hydroxide, and 30 cc. of water, until the solution was evaporated almost to dryness. The residue was then dissolved in 200 cc. of hot water and treated as described above. The yield of 2,4,5-trichlorophenoxyacetic acid was 5.5 g. (85%); recrystallized from benzene, m. p. 153°; white odorless crystals, almost insoluble in water.

Anal. Calcd. for C₈H₅O₂Cl₃: Cl, 41.63; neut. equiv., 255.5. Found: Cl, 41.57; neut. equiv., 256.

THE C. B. DOLGE COMPANY
WESTPORT, CONN.

ROBERT POKORNY

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