conditions at total reflux gave a column efficiency of over 100 plates. About 10% of the distillate boiled below 200°. This included some material boiling at 119–121° which had a refractive index of n^{20}_D 1.4250 (probably dimethylcyclohexane).[4] The main fraction (A) was collected over 0.2° range and after some intermediate fractions, a second large fraction (C) was collected at a higher temperature. The properties of these fractions and some pertinent data of the Russian workers are given in Table I.

TABLE I

ISOMERIZATION OF DICYCLOHEXYL

	% Yield	B. p., °C. 750 mm. press.	n^{20}_D	d^{20}_4
		Russian workers		
Dicyclohexyl		234	1.4807	0.8840
Isomerized main fraction	75	217–219	1.4663	.8592
		Present authors		
Dicyclohexyl		238	1.4696	
Isomerized fraction A	23	215.5–215.7	1.4629	.8512
Isomerized fraction C	8	222–225	1.4701	.8644

Fraction A, containing 885 g. of material, on cooling to 0° partly solidified. The crystalline material was separated (189 g.) and the index of refraction of the filtrate was n^{20}_D 1.4631. Cooling the filtrate to −10° gave a second crop of crystals (96 g.) which was separated by filtration. The mother liquor still had an index of refraction of n^{20}_D 1.4631 and now had a density of d^{20}_4 0.8516. The combined solid material was recrystallized several times from methanol until a constant melting point was reached. The properties of this compound, presumed to be 2,2′-dimethyldicyclopentyl,[4,5] were accurately determined. *Anal.*[6] Calcd. for $C_{12}H_{12}$: C, 86.66; H, 13.34. Found: C, 86.6; H, 13.4; melting point 45.5–45.7° (cor.); boiling point (760) 216.9° (cor.); n^{50}_D 1.4500; n^{60}_D 1.4463. The density and refractive index of this compound in pure dodecane were determined at 20° at different concentrations. The straight-line plot, extrapolated to 100% 2,2′-dimethyldicyclopentyl, gave n^{20}_D 1.4595 and d^{20}_4 0.8492.[7] The infra-red absorption spectrum of the solid is given in Fig. 1.[8]

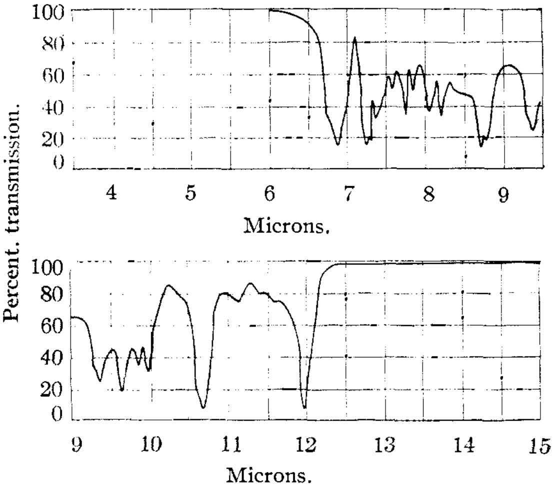

Fig. 1.—Infra-red absorption spectrum: 2,2′-dimethyldicyclopentyl as solid; cell length, 0.1 *mm*.

Fraction C was redistilled and the properties of the middle cut were determined. These were as follows: *Anal.*[6] Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.2; H, 13.2; n^{20}_D 1.4705; d^{20}_4 0.8683; boiling point (760) 224.4° (cor.). These properties are in good agreement with the following properties reported for 1-cyclohexyl-2-methylcyclopentane by Zelinskiĭ and co-workers[9]: b. p. (744 mm.) 225.5–227°; n^{20}_D 1.4701; d^{20}_4 0.8680.

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[6] Analysis by the Coal Analysis Section, Bureau of Mines, U. S. Dept. of the Interior.

[7] The authors wish to thank Mr. Irving Wender and Miss Mary C. Gray for the determination of many of the constants.

[8] This absorption spectrum was kindly determined by Dr. R. A. Friedel of this Laboratory.

[9] Zelinskiĭ, Shuĭkin and Fateev, *J. Gen. Chem. U. S. S. R.*, **2**, 671 (1932).

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Preparation of Vanillic Acid Amide from Vanillonitrile[1]

BY D. M. RITTER

Common methods[2] such as the ammonolysis of methyl vanillate and cautious treatment of vanillonitrile with concentrated mineral acids[3] have failed to give vanillic acid amide. This catalog of unsuccessful efforts includes treatment with mildly alkaline hydrogen peroxide,[4] a reaction which serves to convert to the corresponding amides even highly hindered ortho substituted nitriles.

To obtain vanillic acid amide an indirect method was employed in which the nitrile was converted to vanillic acid *n*-butyl amido ester chloride. The latter compound was easily pyrolyzed to the amide in a reaction developed by Pinner[5] for the synthesis of malonic ester amide.

Experimental[6]

Vanillin Oxime.—The compound was prepared in nearly quantitative yield using the procedure of Lach,[7] modified by omitting the use of alcohol as part of the solvent. Recrystallized from water gave a m. p. 121–122.5°.

Acetovanillonitrile.—Vanillin oxime was converted to the acetylated nitrile by the method of Marcus.[8] The product recrystallized from water and from aqueous ethanol melted at 110°; yield 94%.

Vanillonitrile.—This compound was prepared by dissolving acetovanillonitrile (48 g., 0.25 mole) in 150 cc. of concentrated hydrochloric acid at 60–70° and cooling immediately. The product deposited when the acid solution was poured into 1 liter of water, neutralized to *p*H 4–5 with sodium hydroxide and cooled. It was collected on a filter, washed with water and dried over barium oxide. The yield was 25–26 g. of white needles or 70% of the theoretical quantity, m. p. 86–87°.[8]

Vanillic Acid *n*-Butyl Amido Ester Chloride.—For preparation of the amido ester vanillonitrile (46 g., 0.31 mole) was dissolved in 150 cc. of anhydrous diethyl ether and absolute *n*-butanol (23 g., 0.31 mole) was added. The solution was cooled in an ice-salt-bath and saturated with

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[1] Presented before the Organic Section, Northwest Regional Meeting of the A. C. S., October 29, 1945.

[2] Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1936, p. 250.

[3] Cold sulfuric acid more concentrated than 25 *N* sulfonates vanillonitrile as will be described in another communication.

[4] McMaster and Langreck, THIS JOURNAL, **39**, 103 (1917); McMaster and Noller, *J. Indian Chem. Soc.*, **12**, 652 (1935).

[5] Pinner, *Ber.*, **28**, 479 (1895).

[6] All melting points are uncorrected.

[7] Lach, *Ber.*, **16**, 1786 (1883).

[8] Marcus, *ibid.*, **24**, 3654 (1891).

dry hydrogen chloride (92 g.). After the mixture had stood for three days at room temperature, the solid which had separated was collected on a filter, washed with ether and dried *in vacuo* over barium oxide. The yield was 66.5 g. or 83% of the amount expected from a quantitative reaction. The salt can be prepared from acetovanillonitrile but the yields are variable and often low (27–64%). When well washed with ether and completely freed of hydrogen chloride, the salt obtained directly from the reaction was found to be of high purity. Recrystallization can be carried out from boiling 90% aqueous acetone. The white microcrystals melt between 140 and 150° with decomposition depending upon the rate of heating.

Anal. Calcd. for $C_{12}H_{18}O_3NCl$: Cl, 13.56. Found: Cl, 13.56, 13.35.

Vanillic Acid Amide.—Vanillic acid *n*-butyl amido ester chloride (43.4 g.) was heated in a Claisen flask through which a stream of nitrogen was flowing. When the heating bath temperature reached 140–145° the decomposition began and continued smoothly while the external temperature was raised to 160–170°. *n*-Butyl chloride (12.9 g., b. p. 78°) was gradually produced. Absence of bubbling in the melt indicated the reaction had ceased. The contents of the flask was crystallized from ethanol and from water. The reaction yielded 26.5 g. of white needles m. p. 153–154°, 95% of the vanillic acid amide expected from a quantitative reaction. The yield of *n*-butyl chloride was 83.5%.

Anal. Calcd. for $C_8H_9O_3N$: N, 8.34. Found: N, 8.33, 8.34.

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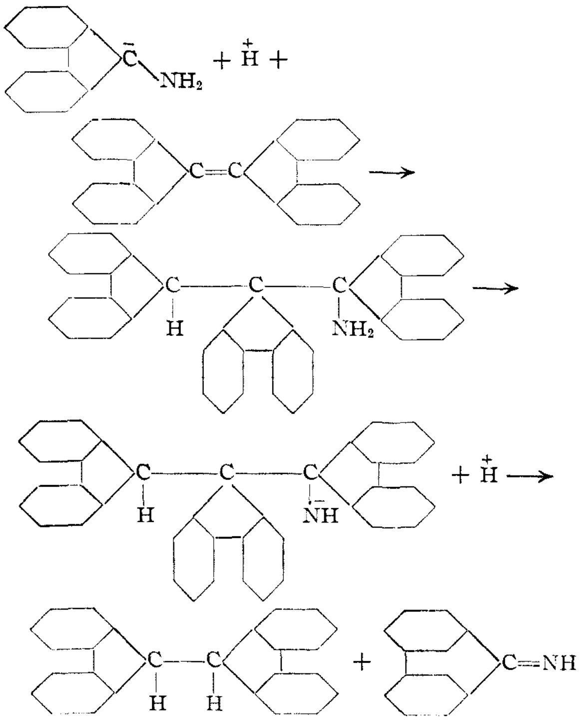
The Dehydrogenation of 9-Aminofluorene and Fluorenol by Unsaturated Compounds. A Michael Condensation

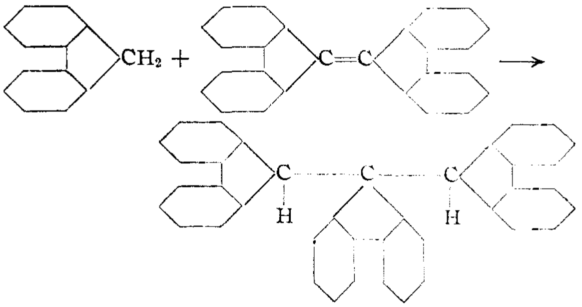
BY LOUIS A. PINCK AND GUIDO E. HILBERT[1]

In retrospect of several studies reported by Pinck and Hilbert[2] dealing with reactions of fluorene, 9-substituted fluorenes and dibiphenylene-ethylene in liquid ammonia and in other alkaline media, the following conclusions are obtained: (1) In an alkaline medium fluorene dissociates into a fluoryl ion and a proton. (2) The lability of the hydrogen atom at the 9 position in 9-aminofluorene is greater than that of the hydrogen atom in the amino group; this of course presupposes that the amino hydrogen is also labile. Its corollary is that the hydrogen atom at the 9 position in 9-fluorenol has a greater lability than the hydrogen in the hydroxy group. (3) The great reactivity of the double bond in dibiphenylene-ethylene suggests that its electronic configuration is more like that of the ethylenic linkage with an adjacent carbonyl group than that of the normal type in ethylene.

On basis of these deductions we are now in a position to postulate a likely reaction mechanism for the dehydrogenation of 9-aminofluorene by dibiphenylene-ethylene and other reactive unsaturated compounds.[3] Starting with ionized 9-aminofluorene the mechanism may be presented by the following equations



1-Aminotribiphenylene-propane is assumed to be an unstable intermediate. Its formation and structure, however, are analogous to those of the stable tribiphenylene-propane.[2d]



The proposed mechanism not only illustrates the reaction *per se* but also serves as a general pattern for similar types of dehydrogenation. For example 9-fluorenol should undergo dehydrogenation in a manner similar to 9-aminofluorene. Furthermore this mechanism should apply to other unsaturated compounds previously cited,[3] which are capable of serving as hydrogen acceptors. Finally these reactions should occur in other alkaline media besides liquid ammonia. These deductions have been confirmed experimentally. Since reactions of 9-aminofluorene with dibiphenylene-ethylene, benzalfluorene, indigo, methylene blue and azobenzene in liquid ammonia had been previously reported, only a

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[2] Pinck and Hilbert, THIS JOURNAL, (a) **57**, 2398 (1935); (b) **68**, 377 (1946); (c) **68**, 867 (1946), (d) **68**, 2014 (1946).

[3] Pinck and Hilbert, *ibid.*, **54**, 710 (1932).