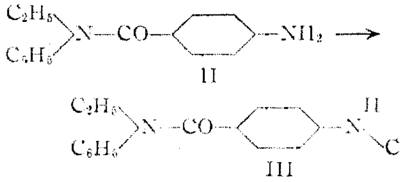

II

III

Since only a small amount of the pure compound was required, no attempt has been made to improve the methods which are described below.

Experimental Part

Stem corrections were applied to melting points all of which were taken in melting point tubes in an electrically heated copper block.

4-Nitro-N-ethyl-N-phenylbenzamide (I).—To the vigorously stirred mixture of 22.0 g. of anhydrous potassium carbonate and a solution of 30.0 g. of 4-nitrobenzoyl chloride[2] in 100 ml. of ethyl ether, there was added slowly at room temperature a solution of 20.0 g. of Eastman Kodak Co. White Label N-ethylaniline. After addition was complete, the mixture was refluxed for thirty minutes and then the ether was evaporated in a stream of air. After the yellow residue had been heated to about 70° so that it became light orange in color and free N-ethylaniline was evident by its odor, it was washed with two 100-ml. portions of 3 *N* hydrochloric acid and finally with a large volume of water on the filter. The crude air-dried product weighed 42.5 g. (yield 97%) and melted at 111–114°. Material which had been twice recrystallized from ethanol melted at 119.5–120.5° and gave the following analysis.

Anal. Calcd. for $C_{15}H_{14}O_3N_2$: C, 66.64; H, 5.22; N, 10.37. Found: C, 66.34; H, 5.31; N, 10.36.

4-Amino-N-ethyl-N-phenylbenzamide (II).—The reduction of (I) followed essentially the procedure of "Organic Syntheses."[3] In a flask which was fitted with a reflux condenser and a mercury-sealed stirrer, 20.0 g. of crude (I), 20 ml. of 95% ethanol, 12 ml. of water and 18.0 g. of iron powder were mixed. After refluxing temperature had been attained, 1.5 ml. of 12 *N* hydrochloric acid in 3.5 ml. of 95% ethanol was added gradually with vigorous stirring, and the refluxing and stirring were continued for three hours. The acid was neutralized with 0.75 g. of sodium hydroxide in 20 ml. of ethanol and the precipitated iron compounds were filtered from the warm solution with the help of a layer of filter aid. Reaction flask and filter cake were washed with two 50-ml. portions of 95% ethanol. The product was isolated by cooling and then by concentration of the solution; the first two crops of white crystals weighed 9.6 g. and had a melting point of 161–162° which was not altered by recrystallization from ethanol. Further concentration and final dilution with water yielded 3.5 g. of less pure material of melting point 159.5–160.5°; the total yield was 13.1 g. or 74%. Analysis of the purer product gave these results.

Anal. Calcd. for $C_{15}H_{16}ON_2$: C, 74.94; H, 6.74; N, 11.93. Found: C, 75.11; H, 6.47; N, 11.76.

4-(N-Ethylamino)-N-ethyl-N-phenylbenzamide (III).—The ethylation of (II) was carried out by means of acetaldehyde–ammonia in the presence of zinc and sulfuric acid according to the procedure of G. Lockemann.[4] A 9.2-g. sample of (II), 100 ml. of ethanol, 340 ml. of water, 38 g. of concd. sulfuric acid and 38 g. of zinc dust were placed in a flask which was provided with a reflux condenser and an addition funnel. Then 2.5 g. of freshly prepared acetaldehyde–ammonia in 80 ml. of water was added to the refluxing solution in the course of forty minutes and refluxing was continued for one hour. The solution was filtered, made alkaline with 120 ml. of 15 *N* ammonium hydroxide, and kept at 5° for two days. The light tan crystalline precipitate was washed with three 50-ml. portions of 6 *N* ammonium hydroxide and a large quantity of water and was crystallized 5 times from ethanol and once from ethanol–water (approximately 1:1). The final product weighed 1.0 g. (yield 10%) and melted at 132.0–132.5°. Three grams of impure material were recovered from the mother liquors. Analysis of the purer sample yielded these results.

Anal. Calcd. for $C_{17}H_{20}ON_2$: C, 76.06; H, 7.53; N, 10.44; mol. wt., 268. Calcd. for $C_{19}H_{24}ON_2$ (the diethylamino compd.): C, 76.97; H, 8.17; N, 9.45; mol. wt., 296. Found: C, 76.03, 75.88; H, 7.50, 7.36; N, 10.42, 10.57; mol. wt., 272 (by Rast micro-method in cyclopentadecanone).

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 4, CALIF.

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[2] Prepared essentially by the method of "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 394.

[3] Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 160.

[4] G. Lockemann, *Chem. Zentr.*, **101**, II, 982 (1930).

Vapor Pressure of *cis*-2-Pentene, *trans*-2-Pentene and 3-Methyl-1-butene

BY DONALD W. SCOTT AND GUY WADDINGTON

A previous publication from this Laboratory[1] reported vapor pressure measurements on 1-pentene, 2-methyl-1-butene and 2-methyl-2-butene. Similar studies have now been made of the remaining three pentene isomers, *cis*-2-pentene, *trans*-2-pentene and 3-methyl-1-butene. The samples used for these measurements were API–NBS hydrocarbons made available by the American Petroleum Institute and the National Bureau of Standards through A.P.I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons."[2]

The differences between the boiling and condensation temperatures observed for these samples at atmospheric pressure were: *cis*-2-pentene, 0.002°; *trans*-2-pentene, 0.001°; 3-methyl-1-butene, 0.006°. The purity of the compounds, as determined by a study of the melting points as a function of fraction melted, has been reported.[3] The vapor pressures were measured by an ebulliometric method. The apparatus described previously[4] was used after making certain modifications to adapt it for measurements with low-boiling materials. The section of the sample ebulliometer containing the thermometer-well for observing condensation temperatures was cooled by surrounding it with a coil of copper tubing through which was circulated an ethylene glycol–water mixture from a refrigeration unit. This same refrigerant was used in the condenser of the sample ebulliometer. Two liquid air traps were used to prevent diffusion of sample vapor into the water ebulliometer. Dry helium gas was used for the inert atmosphere in the apparatus.

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[1] Scott, Waddington, Smith and Huffman, THIS JOURNAL, **71**, 2767 (1949).

[2] The samples were purified at the National Bureau of Standards by the A.P.I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons" under the supervision of Frederick D. Rossini, from material supplied by the following laboratories: *cis*-2-pentene and *trans*-2-pentene, by the A.P.I. Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under supervision of Cecil E. Boord; 3-methyl-1-butene, by the Houdry Process Corporation through the courtesy of E. A. Smith.

[3] Todd, Oliver and Huffman, THIS JOURNAL, **69**, 1519 (1947).

[4] Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, *ibid.*, **71**, 797 (1949).

TABLE I

VAPOR PRESSURES IN MM.

Water		*cis*-2-Pentene		*trans*-2-Pentene		3-Methyl-1-butene	
B. p., °C.	p^a	B. p., °C.	p, calcd.	B. p., °C.	p, calcd.	B. p., °C.	p, calcd.
65	187.57	1.595	187.58	1.026	187.56		
70	233.72	6.522	233.74	5.956	233.74		
75	289.13	11.486	289.12	10.922	289.15		
80	355.22	16.494	355.21	15.927	355.22	0.218	355.25
85	433.56	21.541	433.50	20.969	433.49	5.112	433.53
90	525.86	26.633	525.81	26.055	525.78	10.053	525.86
95	633.99	31.766	633.94	31.183	633.93	15.033	633.94
100	760.00	36.944	760.03	36.354	760.03	20.061	760.00
105	906.06	42.161	906.11	41.561	906.09	25.128	906.00
110	1074.6	47.423	1074.7	46.813	1074.7	30.245	1074.6
115	1268.0	52.724	1268.1	52.100	1267.5	35.402	1268.1
120	1489.1	58.070	1489.3	57.430	1489.2	40.602	1489.2
125	1740.8	63.456	1740.8	62.803	1740.8	45.847	1740.7
130	2026.0	68.882	2025.6	68.211	2025.7	51.139	2025.9

[a] These values of the pressures corresponding to the observed boiling temperatures of water are from the tables of Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

TABLE II

CONSTANTS OF ANTOINE EQUATIONS AND NORMAL BOILING POINTS

	A	*B*	*C*	N. b. p., °C.
cis-2-Pentene	6.87540	1069.466	230.786	36.94
trans-2-Pentene	6.90575	1083.987	232.965	36.35
3-Methyl-1-butene	6.82618	1013.474	236.816	20.06

The results of the measurements are presented in Table I. The data were fitted by least-squares adjustments to Antoine equations of the form, $\log_{10}p = A - B/(t + C)$, where p is the vapor pressure in mm. and t is the temperature in °C. The constants of the equations so obtained and the normal boiling points of the compounds computed from these equations are listed in Table II. Values of the vapor pressure calculated by means of the Antoine equations are given in Table I, columns 4, 6 and 8 for comparison with the experimental values in column 2.

THERMODYNAMICS LABORATORY
PETROLEUM EXPERIMENT STATION
BUREAU OF MINES
BARTLESVILLE, OKLAHOMA

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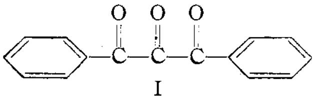
The Chemistry of Vicinal Tricarbonyl Compounds. I. Condensation Reactions of 1,3-Diphenylpropanetrione-1,2,3[1]

BY DEXTER B. SHARP AND HENRY A. HOFFMAN

Perkin–Knoevenagel type condensations have been limited largely to the use of aldehydes as carbonyl components, although a few examples[2] appear in the literature in which simple ketones have been used, most successfully by employing the Doebner[3] modification. Only minor attention has been given to condensations of vicinal polyketones with active-methylene compounds. Schmitt[4] reported a condensation of mesoxalic ester with ethyl cyanoacetate and Sachs and coworkers[5] reported similar condensations of pentanetrione-2,3,4 with pentanedione-2,4, malonic ester and p-nitrophenylacetonitrile. The latter compound was condensed also with 1-(2′-methoxyphenyl)-butanetrione-1,2,3. In no case were structure proofs reported, the structures of the products being assumed, apparently, from analytical data alone.

The present work was undertaken in order to study the condensations of active methylene compounds with 1,3-diphenylpropanetrione-1,2,3 (I),



I

the latter not having been studied in this manner. Malonic acid was employed as the principal methylene component for the twofold reason that it had not been condensed previously with vicinal tricarbonyl compounds and that structure studies of any product would be facilitated by the presence of the carboxyl functions. Structure studies were necessary to determine whether the carbon skeletons of the addenda were unchanged or had undergone rearrangement in a manner similar to that reported by Kohler and Erickson.[6] They isolated the benzoate of benzoin from the equimolar reaction of phenylmagnesium halide with I. The two reactions would be comparable if it were assumed that each involved an attack upon carbonyl carbon by the nucleophilic particles,

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[1] Abstracted in part from a thesis presented by Henry A. Hoffman to the Graduate Faculty of Kansas State College in partial fulfillment of the requirements for the degree, Doctor of Philosophy, granted in January, 1950. Supported in part by a grant-in-aid from the Frederick Gardner Cottrell funds of Research Corporation.

[2] Johnson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 222.

[3] Doebner, *Ber.*, **33**, 2140 (1900); **35**, 1137 (1902).

[4] Schmitt, *Compt. rend.*, **140**, 1400 (1905).

[5] Sachs and Barschall, *Ber.*, **34**, 3047 (1901); Sachs and Rohmer, *ibid.*, **35**, 3307 (1902); Sachs and Wolff, *ibid.*, **36**, 3221 (1903); Sachs and Herold, *ibid.*, **40**, 2714 (1907).

[6] Kohler and Erickson, THIS JOURNAL, **53**, 2301 (1931).