TABLE I

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF FIVE ISOMERIC METHYL-*t*-BUTYLCYCLOHEXANES

Isomer	B. p., °C. (760 mm.)	M. p., °C.	d^{20}, g./ml.	$n^{20}D$	Yield,[d] %	Heat of combustion,[e] kcal./mole	Analyses, %	
							C[f]	H[g]
1,2-[a]	193.67	−60.20	0.83151	1.4565	100	1609	85.85	14.15
1,3-[b]	184.09	−46.11	.80829	1.4460	75	1602	85.74	14.36
1,3-[c]	187.58	−66.02	.81757	1.4486	25	1602	85.80	14.40
1,4-[b]	186.72	−51.04	.80252	1.4418	58	1597	85.27	14.31
1,4-[c]	188.74	−35.03	.81718	1.4487	42	1603	85.85	14.29

[a] Obtained in relatively low purity as indicated by melting curve. [b] Low boiling isomer. [c] High boiling isomer. [a] Relative yield of each isomer not including small amounts of aromatic hydrocarbons found in end cuts. [e] Experimental net values obtained by use of a Parr oxygen bomb calorimeter and following the procedure in ASTM Designation D240-39. [f] Calculated 85.63%. [g] Calculated 14.37%.

obtained. None of these compounds has been previously described in the literature.

In connection with the 1,2-compound, it was of special interest to observe the effect of a highly branched group on the formation of the *cis* and *trans* isomers. Theoretically, due to steric hindrance, it is quite probable that only one isomer may be obtained exclusively or at least in predominant yield. As shown in Table I, apparently only one isomer was obtained since the product had a constant refractive index value throughout the entire distillation range. No definite conclusions can be reached, however, since a high degree of purity could not be obtained despite several attempts at purification described below. In this particular case, the difficulty may readily be attributed to the proximity of boiling points coupled with the similarity of structure in the possible isomers. The melting-point method was used in the evaluation of purity and the remaining two pairs of geometric isomers are reported in rather high purity (above 97 mole per cent.).

Since the appropriate thermodynamic properties have not been investigated, no specific assignment can be made at this time with reference to the definite identification of the *cis* and *trans* configurations. It has been shown[2,3] that the general application of von Auwers' rule[4] is susceptible to error as indicated by the recent change in the name of the *cis* and *trans* isomers of 1,3-dimethylcyclohexane. Accordingly, the products isolated by fractionation are referred to in Table I as the low and high boiling isomers. The physical properties were determined by methods previously described[5] with the exception of the density values which were measured using the apparatus and procedure described by Forziati, *et al.*[6]

Experimental[7]

Materials and Procedure.—The aromatic hydrocarbons used in this investigation had physical properties identical with those previously reported.[1] The hydrogenation charges were 425 g. (2.87 moles), 688 g. (4.64 moles) and 931 g. (6.28 moles) for the *o*-, *m*- and *p*- compounds, respectively. The volume of methylcyclohexane used as solvent was equal to that of the hydrocarbon in each case and 20% by weight of U.O.P. nickel was used as catalyst. Hydrogenation occurred at 170-190° at approximately 1500 p.s.i. and was essentially quantitative.

Purification.—The separation of the isomers was effected by fractionation using a seven-foot Podbielniak column rated above 100 theoretical plates. Subsequent purification, where necessary, consisted of azeotropic distillation with Methyl Carbitol and all the products were passed through silica gel columns prior to the determination of physical properties.

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(2) Pitzer and Beckett, *ibid.*, **69**, 978 (1947).

(3) Rossini and Pitzer, *Science*, **105**, 647 (1947).

(4) von Auwers, *Ann.*, **420**, 92 (1920).

(5) Gibbons, *et al.*, THIS JOURNAL, **68**, 1130 (1946).

(6) Forziati, Mair and Rossini, *J. Research Natl. Bur. Standards*, **35**, 513 (1945).

(7) Macro analyses and heats of combustion by Mr. A. M. Busch and physical properties by Mr. J. F. Thompson of this Laboratory.

Light Absorption of Aqueous Hydrogen Peroxide Solutions in the Near Ultraviolet Region[1]

BY ROBERT C. TAYLOR AND PAUL C. CROSS

It is well established that the ultraviolet absorption spectrum of hydrogen peroxide in aqueous solution consists of a continuum with no evidences of structure extending from about 3800 Å. out to beyond 2000 Å. However, there has been some disagreement as to the exact magnitude of the absorption coefficients, and data in the range between 3200 and 3800 Å. are rather meager. Moreover, the most concentrated solution for which data are available is only about 35% by weight. In connection with other work, the ultraviolet absorption of 50 and 91% by weight solutions of hydrogen peroxide in water has been measured in the region from 2700 to 3800 Å. and the data are reported here.

Experimental.—The source of hydrogen peroxide was 90% material of high purity donated by the Buffalo Electrochemical Company. Before use it was made 0.003 normal in sodium hydroxide and distilled *in vacuo* under its own vapor pressure. By maintaining the liquid at 30° and cooling the receiver in dry ice–isopropyl alcohol, one may distill the solution without ebullition and thus preclude the carry-over of dust and spray particles. The solutions were diluted when necessary with redistilled dust-free water. Analysis of the solutions was carried

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(1) This work was supported in part by the Office of Naval Research under Contract N6ori-88, Task Order No. 1.

out by diluting a small, weighed sample and titrating with potassium permanganate by a procedure very similar to that described by Huckaba and Keyes.[2] Conversion from weight per cent. to concentration in terms of moles per liter was made using the density data of the same authors.[3] To minimize effects due to decomposition by the ultraviolet light, samples were changed frequently. In all cases, analysis showed that the percentage decomposition which did occur during an exposure was entirely negligible.

The amount of absorption was determined using a Hilger Sector Photometer and standard photographic procedures. Both continuous and discontinuous light sources were employed in taking the spectra, and density comparisons were made with the aid of a microdensitometer. Previous workers progressively diluted their samples as they approached shorter wave lengths so as to maintain a measurable transmission; in this work, the alternative procedure was employed in which the cell length was progressively shortened while the concentration remained fixed.

Results and Discussion.—The experimental results for both the 50 and 91% solutions are given in Table I.

TABLE I

MOLAR ABSORPTION COEFFICIENTS OF AQUEOUS HYDROGEN PEROXIDE SOLUTIONS

Wave length, Å.	Absorption coefficients 50%	91%
3800	0.0030	0.0022
3700	.0076	.0056
3600	.019	.014
3500	.046	.036
3400	.11	.089
3300	.24	
3200	.53	
3100	1.10	
3000	2.26	
2900	4.6	
2800	9.1	
2700	17.1	

The absorption coefficient, α, is defined in the usual way by the Beer–Lambert Law, $I = I_0e^{-\alpha cd}$. I_0 and I are the incident and emergent intensities, respectively, c is the concentration in moles per liter and d is the path length in cm. Four plates were taken for the 50% solution with an average of seven spectra per plate, the wave length region covered by any one plate partially overlapping those of other plates. In the case of the 91% solution, seven spectra on one plate only were obtained. To prepare Table I, values of log α were plotted *versus* wave length on a large graph. The tabulated absorption coefficients were then read from a smooth curve drawn to give best agreement with the experimental points. The r. m. s. deviations of the experimental points were 8.5% and 5.0% from the respective curves of the 50% and 91% solutions.

The data presented here for the 50% solutions for the most part agree well with those already reported by other workers for more dilute solutions,[4,5,6,7] the chief exception being the values given by Urey, Dawsey and Rice[7] which deviate appreciably at the longer wave lengths. In Fig. 1, the data already recorded in the literature are compared graphically with those found in this work. All data have been converted to the basis defined previously.

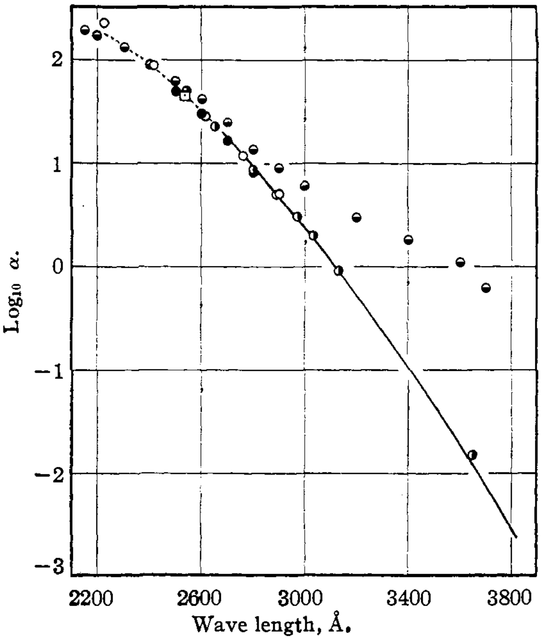

Fig. 1.—Absorption coefficients of aqueous hydrogen peroxide solutions: ○, reference 4; ◑, reference 5; ●, reference 6; ◒, reference 7; □, reference 8; ——, this work.

It will be noted that the absorption coefficients for the 91% solution are appreciably less than those recorded for the more dilute solutions indicating Beer's law is not obeyed at high concentrations. Since evidence by previous workers[6] has been presented showing that the OOH^- ion absorbs ultraviolet light much more strongly than the neutral molecules, a part of the decrease in absorption can be attributed to the smaller amount of dissociation at the higher concentration. The long wave length edge of the absorption given by Urey, Dawsey and Rice as 3800 Å. is in agreement with that found here although such a designation is somewhat arbitrary in that no sharp break is noted in the absorption curve at this point. Instead the absorption

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[2] C. E. Huckaba and F. G. Keyes, THIS JOURNAL, **70**, 1640 (1948).

[3] C. E. Huckaba and F. G. Keyes, *ibid.*, **70**, 2578 (1948).

[4] E. Lederle and A. Rieche, *Ber.*, **62B**, 2573 (1929).

[5] A. J. Allmand and D. W. G. Style, *J. Chem. Soc.*, 596 (1930).

[6] G. Bredig, H. L. Lehmann and W. Kuhn, *Z. anorg. allgem. Chem.*, **218**, 16 (1934).

[7] H. C. Urey, L. H. Dawsey and F. O. Rice, THIS JOURNAL, **51**, 1371 (1929).

merely decreases gradually to a very low value approaching that of water.

The photochemical process giving rise to the continuum has been discussed by Urey, Dawsey and Rice[7] and again recently by Holt, McLane and Oldenberg.[8]

(8) R. B. Holt, C. K. McLane and O. Oldenberg, *J. Chem. Phys.*, **16**, 225 (1948).

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Preparation of Tetramethyl Pyrophosphate

BY A. D. F. TOY

Previous investigations[1] have shown that the tetra-alkyl esters of pyrophosphoric acid, with the exception of the methyl ester, may be readily prepared in good yields by the controlled hydrolysis of the dialkyl chlorophosphates in the presence of pyridine. It has now been found that tetramethyl pyrophosphate may be prepared in the pure state and in good yield by the action of dimethyl chlorophosphate on trimethyl phosphate with the evolution of methyl chloride.

Procedure.—A mixture of 72.3 g. (0.5 mole) of dimethyl chlorophosphate, 350 g. (2.5 mole or 400% excess) of redistilled[2] trimethyl phosphate ($n^{25}\mathrm{D}$ 1.3948), containing a porous porcelain boiling chip was heated with occasional stirring, in a 500-cc. 3-necked flask equipped with a thermometer, a stirrer and a condenser fitted with a calcium chloride tube. Gaseous evolution began slowly at 105° and became steady at 113°. The temperature was maintained at 113° for two and one-half hours. When the rate of gas evolution slowed down the temperature was raised to 122°. After thirty minutes at 122° gas evolution had practically ceased. A portion of the mixture gave only a faint test for chloride indicating that the reaction had gone essentially to completion. The loss of methyl chloride amounted to 24.3 g. compared with a theoretical loss of 25.3 g. The product was fractionally distilled under reduced pressure and after the removal of the excess trimethyl phosphate (279 g., $n^{25}\mathrm{D}$ 1.3950), the fraction boiling at 106-108° and 0.3 mm., weighed 99.6 g. (85%). The residue weighed 9.5 g. Analysis and toxicity data showed the product to be identical with the tetramethyl pyrophosphate described previously.[1]

When only an equivalent quantity (0.5 mole) of trimethyl phosphate was used a somewhat lower yield of 86 g. (73.5%) of tetramethyl pyrophosphate was obtained. When the higher temperature of 130° was used with the 400% excess of trimethyl phosphate the gaseous evolution was much more rapid and the reaction was complete after one hour and ten minutes, the same high yield (84.3%) being obtained in the shorter time.

It has been previously pointed out,[1] that the analogous reaction between diethyl chlorophosphate and triethyl phosphate does not produce tetraethyl pyrophosphate in satisfactory yield.

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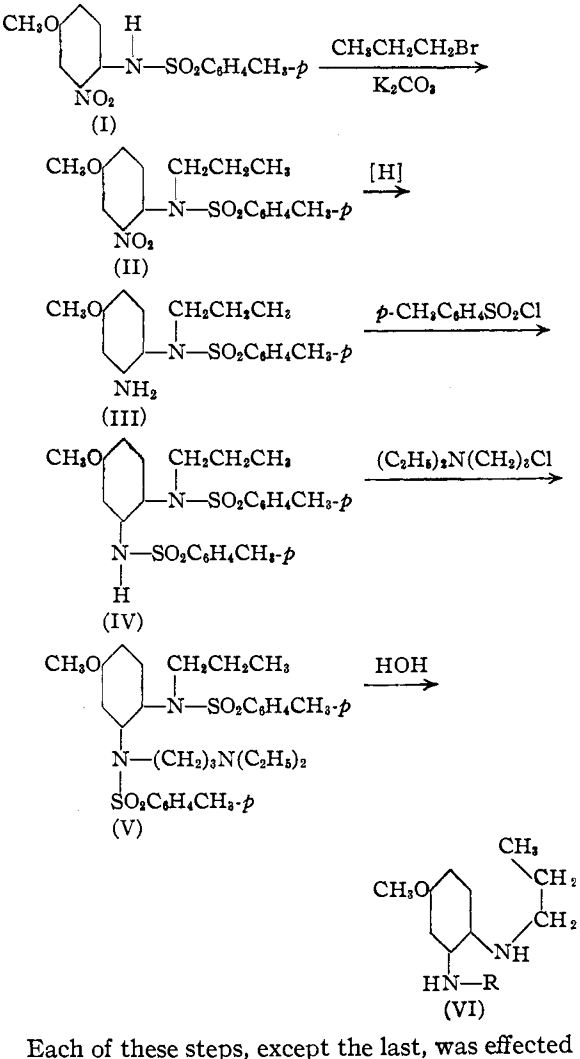
[1] Toy, THIS JOURNAL, **70**, 3882 (1948).

[2] It was necessary to purify trimethyl phosphate by distillation ($n^{25}\mathrm{D}$ 1.3948 to 1.3950). When the regular commercial grade material ($n^{25}\mathrm{D}$ 1.3928), was used without previous purification the gaseous bubbling began at a much lower temperature and only very low yields of tetramethyl pyrophosphate were obtained.

Attempted Synthesis of an Aliphatic Analog of Plasmochin[1]

BY MARTIN J. WEISS AND CHARLES R. HAUSER

Barber, Major and Wragg[2] have recently reported the synthesis of an aliphatic analog (VI, R = $-CH(CH_3)(CH_2)_3N(C_2H_5)_2$) of plasmochin. Before the appearance of this paper we had attempted the synthesis of a similar analog (VI, R = $-(CH_2)_3N(C_2H_5)_2$). Although this analog was not isolated in the pure condition, the reactions employed are of some interest.



Each of these steps, except the last, was effected in good yield. An attempt to propylate 2-nitro-4-methoxyaniline was unsuccessful but the *p*-toluenesulfonamido derivative (I) was readily alkylated. The nitro group of compound (II) was reduced in ethanol with zinc and ammonium chloride. After an unsuccessful attempt had been made to alkylate the amino group of compound

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[1] This work was supported by a grant from the Duke University Research Council.

[2] Barber, Major and Wragg, *J. Chem. Soc.*, 613 (1946).