We have used the chloroacetic acid actinometer together with three thermopiles, two quartz-cadmium photocells, and two Bureau of Standards lamps in an attempt to make an accurate determination of the light flux from a true resonance type source of λ 2537.[4] The thermopiles were of the vacuum quartz type, two constructed with the Bi–Ag couple and one with the Bi–Bi 5% Sn couple. Two had platinum black receivers and one carbon black. These were used in two ways. First, the flux of λ 2537 was measured directly by placing the thermopiles with the elements 6 cm. below the exit window and alternately freezing out with liquid air and resupplying mercury vapor to the resonance lamp. Second, the thermopiles were used to calibrate the photocells using a Hg–He discharge tube from which the fraction of energy emitted at λ 2537 was estimated by filters and spectrograms to be 85% and which had a much greater intensity than the resonance lamp so would give larger thermopile deflections. At least 99% of the deflection with the photocells when using the Hg–He discharge tube was due to λ 2537 as judged by interposing a Corning 986 Corex Red-Purple filter between the source and the photocells on the one hand, and between the source and the spectrograph on the other. The photocell reading was reduced to 2.7% by the filter (5 mm.) and the time of exposure of the spectrum plate had to be increased about thirty times to give the same darkening of the 2537 line. The transmission of this filter according to the curve given by the makers is about 3% at 2537 Å. The resonance lamp gives 99.9% of its line energy at 2537 Å. judging from a series of spectrograms ranging in exposure from one-fourth to two hundred and fifty seconds. The above estimates neglect the possibility of the presence of some radiation at λ 1849. This is absorbed strongly in air and is shown not to be present in appreciable amount by the fact that the intensities from the He–Hg discharge tube as measured by the photocell obeyed closely the inverse square law up to 80 cm. in air, the largest distance tried.

The average of ten determinations involving various combinations of the above instruments gave 5.93 × 10^{12} quanta per sq. cm. per second at 6 cm. from the resonance lamp exit window, per unit photocell current. A photocell was used at all times with the resonance lamp as a check on the constancy of its intensity. The mean deviation among these ten values was 5% from the above value. Exposures were made in a quartz cylindrical vessel 8 mm. in thickness placed 6 cm. below the exit window. The vessel was filled with 1 M acid and exposed for periods of about five hours. During exposure the intensity of the lamp was followed with the photocell. Exposed and unexposed samples were run consecutively for chloride ion by electrometric titration with standard silver nitrate using the calomel and silver–silver chloride electrodes. The e. m. f. $vs.$ volume of silver nitrate curves were plotted together and the amount of chloroacetic acid hydrolyzed by the light was read from the difference along the volume axis between the two curves at the inflection point. Microburets were used and the above differences amounted to about 0.6 ml. of 0.000864 N silver nitrate. The normality of the silver nitrate checked well against standard potassium chloride solution by the titration method used.

The quantum yields at 26° on the two samples

run were 0.332 and 0.352. The average of these, 0.342, is to be compared to the value 0.33, read from the curve of Smith, Leighton and Leighton for 26°. The agreement is within the errors of measurement in either experiment.

CHEMISTRY LABORATORY
THE UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI   RECEIVED MAY 6, 1940

NEW COMPOUNDS

DIMETHYLETHYLPHENYLAMMONIUM BROMIDE

Dimethylaniline was allowed to react with ethyl bromide in the cold for a few days. The product recrystallized from absolute alcohol and ethyl acetate gave fine glistening needles which sublimed at 193–194° (uncor.) and turned slightly blue on standing, presumably through oxidation. This substance has already been mentioned[1] as formed from dimethylaniline and ethyl bromide but no analysis or statement of its properties has been given.

$Anal.$ Calcd. for $C_{10}H_{16}NBr$: C, 52.18; H, 7.01; N, 6.09; Br, 34.71. Found: C, 52.42; H, 7.16.

This work was done at the suggestion and under the direction of Dr. Alexander E. Knoll of Columbia University. The carbon and hydrogen analysis was performed in Dr. Knoll's laboratory by Mr. S. Gottlieb.

(1) $Gazz. chim. ital.$, **42**, 425–437 (1912).

929 WEST END AVENUE   ARTHUR KANT
NEW YORK, N. Y.
                    RECEIVED APRIL 16, 1940

BENZAL-2,4,6-TRIBROMOANILINE

Benzal-2,4,6-tribromoaniline was prepared by heating equivalent parts of benzaldehyde and 2,4,6-tribromoaniline; m. p. 94–95° after two crystallizations from alcohol.

$Anal.$ Calcd. for $C_{13}H_8NBr_3$: Br, 57.3. Found: Br, 57.1.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS   W. S. EMERSON
URBANA, ILLINOIS   F. C. UHLE
                    RECEIVED MAY 1, 1940

ACETYLENIC CYCLOHEXANE DERIVATIVES

1 - (3 - Methyl - 1 - pentyn - 3 - ol) - 2 - methylcyclohexanol.—To the Grignard reagent prepared from 24 g. of magnesium, 115 g. of ethyl bromide and 200 ml. of anhydrous ether was added with stirring a solution of 69 g. (0.5 mole) of 1-ethynyl-2-methylcyclohexanol[1] in 100 ml. of anhydrous ether as rapidly as possible without loss of ether. The solution was stirred for one hour after all the

(1) Cook and Lawrence, $J. Chem. Soc.$, 58 (1938).

acetylenic carbinol had been added and 36 g. (0.5 mole) of ethyl methyl ketone was dropped in. The mixture was stirred for two hours longer and poured into a mixture of 90 ml. (1.1 moles) of concentrated hydrochloric acid and 200 g. of ice. After the magnesium hydroxide had dissolved, the layers were separated, the water layer extracted with ether. After drying the ether solution over anhydrous sodium sulfate, the solvent was removed by distillation. The residue was heated in an an oil-bath to 110° under 18 mm. of pressure to remove volatile material. The residue was recrystallized from petroleum ether (b. p. 30–60°). The product was deposited from the petroleum ether in white needles melting at 69–70° and weighed 57 g. (53% of the theoretical).

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.29; H, 10.48. Found: C, 73.85, 73.71; H, 10.17, 10.24.

1 - (3 - Methyl - 3 - penten - 1 - ynyl) - 2 - methylcyclohexene.—Twenty-two and five-tenths grams of the glycol was dehydrated by heating with 6 g. of potassium bisulfate to 180° in an oil-bath for ten minutes. Water was removed by distillation at 18 mm. pressure. The 1-(3-methyl-3-penten-1-ynyl)-2-methylcyclohexene was distilled at 2 mm. pressure. The yield was 17 g. (90%) of a product boiling at 82–84° (2 mm.). Due to rapid absorption of oxygen by the dienyne, the analysis was low in both carbon and hydrogen, as is usually the case with closely related compounds.[2]

Anal. Calcd. for $C_{13}H_{18}$: C, 89.66; H, 10.34. Found: C, 87.45; H. 10.05.

2-Methyl-1,1'-dicyclohexanolacetylene.—To the Grignard solution prepared from 106 g. (4.4 moles) of magnesium and 490 g. (4.5 moles) of ethyl bromide in 1.5 liters of anhydrous ether was added 250 g. (2 moles) of 1-ethynyl-

(2) See Marvel, Mozingo and Kirkpatrick, THIS JOURNAL, **61**, 2003 (1939).

cyclohexanol.[2] The solution was stirred for one hour and 280 g. of 2-methylcyclohexanone added as rapidly as possible without loss of ether. The reaction mixture was allowed to stand overnight and poured over ice containing 400 ml. (4.9 moles) of concentrated hydrochloric acid. The product was extracted with ether and the ether solution dried over sodium sulfate. After the low-boiling material had been removed by heating the residue to 100° in an oil-bath and under a pressure of 18 mm., the residue was cooled. Part of the material crystallized on standing. This solid was recrystallized from petroleum ether (b. p. 30–60°) and melted at 94–95°.

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.27; H, 10.17. Found: C, 76.13, 76.55; H, 10.26, 10.13.

The yield of the solid material was low (41% or less) and it apparently was one of the two possible stereoisomers. The glycol mixture underwent dehydration on heating and could not be distilled.

2-Methyl-1,1'-dicyclohexenylacetylene.—The crude 2-methyl-1,1'-dicyclohexanolacetylene from the previous preparation, including the crystals which had been removed, was refluxed for three hours with 500 g. of 40% sulfuric acid. The product was extracted with ether and the ether solution was washed free from acid with dilute sodium carbonate solution. The crude material was fractionated and the portion boiling at 115–117° (2 mm.) collected. The yield was 206 g. (51% of the theoretical based on the 1-ethynylcyclohexanol used); $n^{20}D$ 1.5452.

Anal. Calcd. for $C_{15}H_{20}$: C, 89.93; H, 10.07. Found: C, 89.61; H, 10.24.

(3) Röhm and Haas Post-doctorate Special Research Assistant in Chemistry.

NOYES CHEMICAL LABORATORY   C. S. MARVEL
UNIVERSITY OF ILLINOIS   RALPH MOZINGO[3]
URBANA, ILLINOIS   RALPH WHITE[3]
                    RECEIVED MAY 1, 1940

COMMUNICATION TO THE EDITOR

VITAMIN K ACTIVITY OF CERTAIN NAPHTHOLS AND TETRALONES

Sir:

The observed high antihemorrhagic activity of the 5,8-dihydro and 2,3-oxido derivatives of vitamin K_1 and 2-methyl-1,4-naphthoquinone,[1] coupled with the opportunity for the reversion of these substances to the quinones by simple oxidation or reduction, suggests that the activity is not due to the functioning of the derivatives as such but is a manifestation of their biological transformation into the quinones, with somewhat

(1) Fieser, Tishler and Sampson, THIS JOURNAL, **62**, 996, 1628 (1940).

varying efficiency. As a further test of this hypothesis we investigated 3-methyl-1-naphthol and 2-methyl-1-naphthol, for these naphthols are quite remote from the quinone–hydroquinone type but could yield methylnaphthohydroquinone by hydroxylation. When assayed in chicks by the eighteen-hour method, both substances showed remarkably high antihemorrhagic activity (response at a dosage of 1 γ). In striking contrast is the observation that 1-methyl-2-naphthol, 3-methyl-2-naphthol, and 4-methyl-1-naphthol are all inactive at 1000 γ; these isomers are not convertible into the potent 2-methyl-1,4-naphthoquinone. 2-Methyl-1-naphthylamine is active at