advantages over that of Reichstein and Grüssner[2] and over the two step procedure of Köhn and Neustädter[3] as modified by Stiller, *et al.*,[4] it seemed desirable to publish the details.

Experimental

α,α-Dimethyl-β-hydroxypropionaldehyde.—This compound was prepared by the method of Wesseley,[5] with the exception that the reaction flask was cooled in an ice-bath during the initial vigorous stage of the reaction.

α-Hydroxy-β,β-dimethyl-γ-butyrolactone.—Crude α,α-dimethyl-β-hydroxypropionaldehyde (102 g., 1 mole) was dissolved in 1 liter of water at 60–70°. The solution was cooled under the tap and a cold solution of 133 g. of calcium chloride and 98 g. of potassium cyanide was added rapidly. The flask was stoppered (to exclude carbon dioxide) and was allowed to stand at room temperature with occasional shaking for eighteen hours. The solution was then heated on the steam cone to 70–80° and 151 g. of oxalic acid dihydrate was added. The calcium oxalate was removed by filtration and the filtrate was concentrated to a gum under reduced pressure. It is essential that as much water as possible be removed at this point. The residue was extracted with 1 liter of dry acetone and the insoluble material was removed by filtration. The filtrate was concentrated to a viscous oil under reduced pressure. The oil was taken up in dry acetone and the solution was filtered. The acetone was removed and the residue was fractionated under reduced pressure. The lactone distilled at 125–130° (18 mm.) as an oil which immediately solidified to a glass in the receiver. The yield of lactone, melting at 75–80°, was 100–105 g. (77–81% of the theoretical amount). The *p*-nitrobenzoate of the lactone melted at 137–138° as reported by Stiller, *et al.*[4]

The unusual ease of hydrolysis of the nitrile is interesting in view of the lability of the amide group in pantothenic acid.

(3) Köhn and Neustädter, *Monatsh.*, **25**, 46 (1904).
(4) Stiller, *et al.*, THIS JOURNAL, **62**, 1785 (1940).
(5) Wesseley, *Monatsh.*, **21**, 231 (1930).

DIVISION OF BIOCHEMISTRY
NOYES LABORATORY OF CHEMISTRY
URBANA, ILLINOIS RECEIVED NOVEMBER 1, 1940

Note on the Absorption Spectra of Some Alkyl Chrysenes

BY R. NORMAN JONES

The absorption spectra of 5-methyl,[1] 4,5-dimethyl,[1] 5,6-dimethyl[1] and 4,5-methylenechrysene[2] recently have been determined in these laboratories. The wave lengths and intensities of the various maxima are summarized in Table I and the curves are given in Figs. 1, 2. The experimental technique has been described previously.[3]

The spectra of 5-methyl and 5,6-dimethylchrysene resemble that of the unsubstituted hydrocarbon[4] apart from the usual shift to longer wave lengths and some loss of fine structure. 4,5-Dimethylchrysene differs somewhat from the other two methyl derivatives, the most intense maximum showing some resolution while at longer wave lengths the intensity of absorption is greater and the resolution less.

TABLE I

WAVE LENGTHS (Å.) OF THE MAXIMA AND CORRESPONDING INTENSITIES (LOG E_{molar}) OF THE SPECTRA OF SOME ALKYL AND ALKYLENE-CHRYSENE DERIVATIVES (SOLVENT ETHANOL)

	Max.	Intensity
5-Methylchrysene	2705	4.98
	2865	3.99
	3005	3.98
	3125	4.06
	3265	4.06
	3505	2.89
	3680	2.90
5,6-Dimethylchrysene	2740	4.95
	3040	3.96
	3225	4.08
	3330	4.05
	3550	2.94
	3745	2.84
4,5-Dimethylchrysene	2740	5.10
	2815	5.05
	3120	4.15
	3300	4.34
	3450	4.34
	3800	2.87
4,5-Methylenechrysene	(2590)	4.83
	2655	4.99
	2690	5.04
	3010	4.09
	3130	4.07
	3265	4.09
	3420	2.98
	3465	2.82
	3525	2.65
	3606	2.89

The spectrum of 4,5-methylenechrysene (1) is particularly interesting as in the 1,2-benzanthracene series such a bridge methylene group has been observed to produce a considerable change in the spectrum including an increase in the amount of fine structure resolved.[5] The spectrum of 4,5-methylenechrysene also shows an increase in the amount of fine structure, particularly if comparison is made with 4,5-dimethylchrysene, substituted at the same position (Fig. 2). A corresponding comparison between the dimethyl and the methylene derivative is not possible in the

(1) Compounds kindly supplied by Dr. M. S. Newman: see THIS JOURNAL, **62**, 870 (1940); **62**, 2295 (1940).
(2) Fieser and Cason, *ibid.*, **62**, 1293 (1940).
(3) Jones, *ibid.*, **62**, 148 (1940).
(4) Mayneord and Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935).
(5) Jones, THIS JOURNAL, **63**,151 (1941).

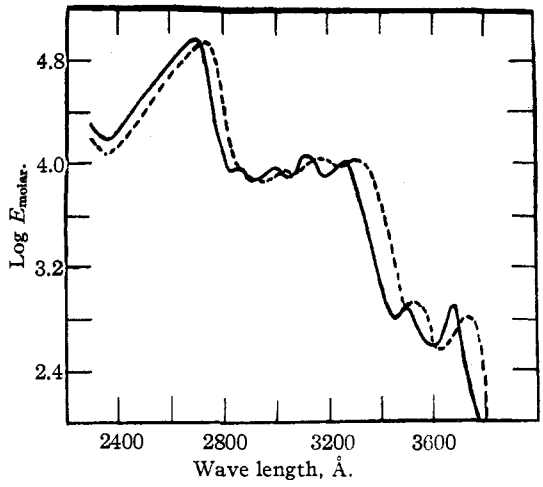


Fig. 1.— ———, 5-Methylchrysene; - - -, 5,6-dimethylchrysene.

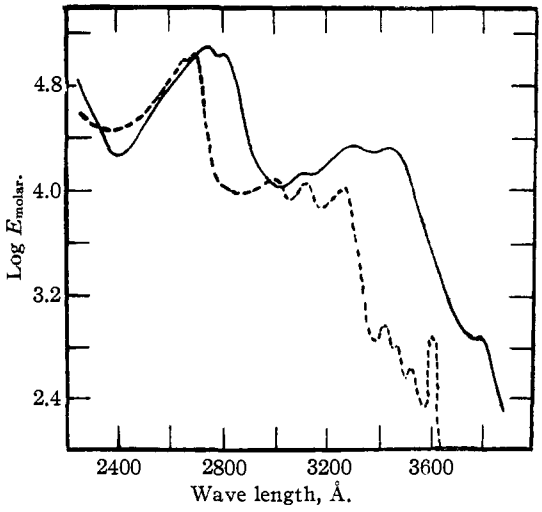
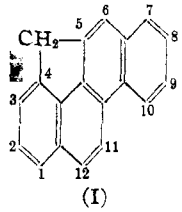


Fig. 2.— ———, 4,5-Dimethylchrysene; - - -, 4,5-methylenechrysene.

1,2-benzanthracene series as all attempts so far made to synthesize 1',9-dimethyl-1,2-benzanthracene have failed.

These variations in structural detail among the spectra, while significant, are not sufficiently great to prejudice the use of absorption spectrophotometry as a means of characterizing the chrysene ring structure.



(I)

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED OCTOBER 19, 1940

The Preparation of N-Allylnormorphine

BY ELTON L. MCCAWLEY, E. ROSS HART AND DAVID FIELDING MARSH

In the course of a biochemorphic survey of morphine derivatives, N-allylnormorphine has been prepared. Using von Braun's method[1] morphine is acetylated with acetic anhydride to protect the hydroxyl groups. The nitrogen-methyl group is removed by the action of cyanogen bromide and decomposition to normorphine. The normorphine base reacts with allyl bromide at 70° to form N-allylnormorphine hydrobromide, m. p. 126°, soluble in water, sl. sol. in alcohol and insoluble in ether; N-allylnormorphine free base melts at 92–93°.

Anal. Calcd. for $C_{19}H_{21}O_3N$: C, 73.3; H, 7.0; mol. wt., 311.2. Found: C, 74.6; H, 7.5 (Kirk); mol. wt., 313 (Rast).

An iodoxybenzoate test indicates a free phenolic hydroxyl group.

The preparation of normorphine by evolution of formaldehyde from morphine oxide and chromic acid and also the decomposition of N-nitrosonormorphine by alcoholic potash are unsatisfactory due to excessive breakdown of the ring structure. These procedures[2] are unsuitable for the preparation of norcodeine, for the same reason.

N-allylnormorphine appears to have a stronger antagonistic action toward the depression of respiration evoked by morphine than N-allylnorcodeine.[3]

(1) Von Braun, *Ber.*, **47**, 2312 (1914).

(2) Diels and Fischer, *ibid.*, **49**, 1721 (1916); Speyer and Walther, *ibid.*, **63**, 852 (1930).

(3) Pohl, *Z. exp. Path. Therap.*, **17**, 370 (1915).

PHARMACOLOGICAL LABORATORIES
JEFFERSON MEDICAL COLLEGE
PHILADELPHIA, PENNSYLVANIA, AND
UNIVERSITY OF CALIFORNIA MEDICAL SCHOOL
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Thioanilides of Malonic Acids

BY AVERY A. MORTON, A. R. OLSON AND J. W. BLATTENBERGER

Phenyl isothiocyanate has been used[1] as a test for organometallic compounds. If reactions of this reagent with amyl- or benzylsodium parallel those observed[2] with carbon dioxide it should be possible to prepare directly the thioanilides of the corresponding malonic acid according to the se-

(1) Sach and Loevy, *Ber.*, **36**, 585 (1903); Schlenk, Bergmann and co-workers, *Ann.*, **463**, 1; **464**, 1 (1928); Gilman and Breuer, THIS JOURNAL, **55**, 1262 (1933).

(2) Morton and Fallwell, Jr., *ibid.*, **60**, 1426 (1938).