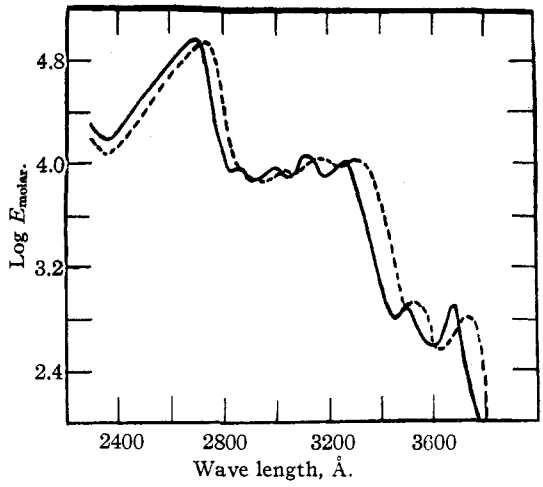


Fig. 1.— ——, 5-Methylchrysene; - - -, 5,6-dimethylchrysene.

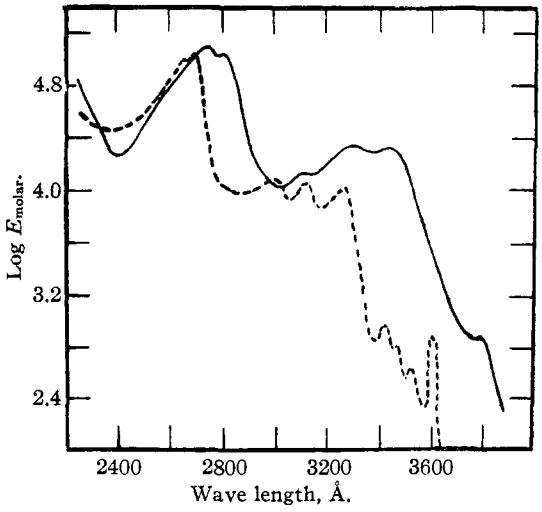
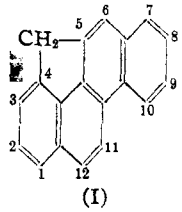


Fig. 2.— ——, 4,5-Dimethylchrysene; - - -, 4,5-methylenechrysene.

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).

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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).

quence of reactions shown below. Small quantities of the expected products were indeed obtained.

$$C_5H_{11}Na \xrightarrow{C_6H_5NCS} C_4H_9CH_2C(=NC_6H_5)SNa \xrightarrow{C_5H_{11}Na}$$
$$C_4H_9CH(Na)C(=NC_6H_5)SNa \xrightarrow{C_6H_5NCS}$$
$$C_4H_9CH[C(=NC_6H_5)SNa]_2 \xrightarrow{HX} C_4H_9CH[CSNHC_6H_5]_2$$

A peculiarity in this preparation was the repeated failure to obtain isolable quantities of either product when a creased flask[3] was used as the reaction vessel. In such cases the product was a material which has not yet been characterized. Increases in yield of 50 to 100% in preparation of certain Grignard reagents and improvement in other reactions have been noted in this Laboratory when the experiments have been carried out in flasks of this special design but this is the first instance where the products appeared different.

Reactions of amylsodium with carbon disulfide, sulfur dioxide, and sulfur trioxide in hope of obtaining various sulfur-containing acids gave mixtures which were not separated readily.

Experiments

Butyldithiomalon Dianilide.—Amylsodium was prepared from 37 g. of *n*-amyl chloride with 20 g. of fine sodium sand in petroleum ether at 0° in an ordinary 3-neck flask arranged in the conventional manner,[4] described before. Phenyl isothiocyanate, 47 g. (0.35 mole) was added dropwise over a period of ten minutes. After stirring for thirty minutes, the mixture was decomposed with 30 ml. of alcohol followed by 150 ml. of water. The two latter were then separated. The aqueous layer was acidified and extracted with ethyl ether and with ethyl acetate. The combined extracts were evaporated to a dark brown non-crystalline solid, and the latter extracted with petroleum ether and with ligroin. Crystals melting from 67 to 68° were obtained.

The organic layer in turn yielded a heavy residual oil on evaporation which was distilled in a Hickman alembic at 5 to 10 microns. The fraction boiling from 100 to 135° slowly crystallized yielding a product identical with the crystals obtained by extraction of the aqueous layer. The combined product was recrystallized from alcohol giving 1.2 g. (2% based on the amyl chloride used) of material melting at 67–68°.

Anal. Calcd. for $C_{19}H_{22}N_2S_2$: S, 18.71; N, 8.19. Found: S, 18.3; N, 8.10.

Upon saponification with excess alkali aniline was evolved and the alkali consumed was equivalent to the above formula. Saponification equivalent calcd., 171; found, 169.

Phenyldithiomalon Dianilide.—Preparation of *n*-amylsodium was carried out as before. Toluene, 33 g., was then added and the mixture refluxed for one hour, after which phenyl isothiocyanate, 47 g., was added dropwise. Decomposition and separation were carried out in the same manner as before. Crystals from the aqueous layer were identical with those obtained from the organic layer by distillation at 2 to 3 microns at 120 to 150°. The combined product was carefully sublimed at 60–80° and 2 microns giving a clean white material melting 66 to 67°; yield 1.5 g. or 2.4% based on the amyl chloride used.

Anal. Calcd. for $C_{21}H_{18}N_2S_2$: S, 17.68; N, 7.74. Found: S, 17.1; N, 7.70. Aniline was detected upon hydrolysis with alkali. Saponification equivalent. Calcd., 181; found, 184.

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CAMBRIDGE, MASS. RECEIVED OCTOBER 22, 1940

(3) Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939).

(4) Morton and Richardson, THIS JOURNAL, **62**, 123 (1940).

The Identity of α- and β-Earleine with Betaine and Choline, Respectively

BY ARTHUR STEMPEL AND ROBERT C. ELDERFIELD

In a previous communication from this Laboratory[1] the isolation of two non-toxic, nitrogenous bases from *Astragalus earlei*, or Big Bend loco weed, was described. These were assigned the empirical formulas $(C_{16}H_{37}N_3O_7)_x$ and $(C_{16}H_{37}N_3O_4)_x$ on the basis of analytical data on their salts and were named α- and β-earleine, respectively. With the limited amount of material at hand it was not possible to characterize the bases further at that time. In the meantime we have secured additional amounts of the weed and have identified the bases as betaine and choline, respectively. A study of the thermal decomposition of "β-earleine" provided the clue for the correct interpretation of its nature, from which the identity of "α-earleine" with betaine was surmised. From the decomposition products of "β-earleine" we have identified trimethylamine and acetaldehyde. A sample of "β-earleine" produced a typical choline effect on white mice when tested in the Parke, Davis laboratories through the kind coöperation of Dr. Oliver Kamm. The names α- and β-earleine should, therefore, be stricken from the literature.

Experimental

Identification of Betaine.—The isolation was carried out as previously described.[1] The picrate melted at 184° and gave no depression in melting point when mixed with betaine picrate.

Anal. Calcd. for $C_5H_{11}O_2N \cdot C_6H_3O_7N_3$: C, 38.2; H, 4.1; N, 16.2. Found: C, 38.3; H, 4.1; N, 15.6.

The styphnate melted at 186–188° (dec.).

(1) Pease and Elderfield, *J. Org. Chem.*, **5**, 192 (1940).