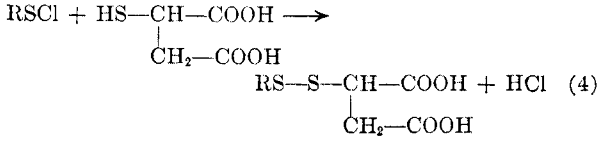
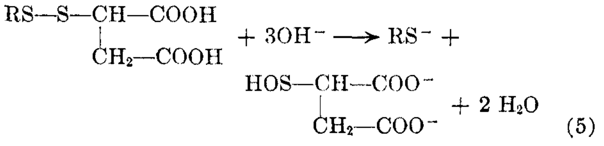


$$\mathrm{RSCl} + \mathrm{HS{-}\underset{\displaystyle |\atop CH_2{-}COOH}{CH}{-}COOH} \longrightarrow \mathrm{RS{-}S{-}\underset{\displaystyle |\atop CH_2{-}COOH}{CH}{-}COOH} + \mathrm{HCl} \qquad (4)$$

Addition of alkali, followed by warming in some cases, dissolves the disulfide and displaces RS^- (Equation 5). Filtration and acidification of the filtrate precipitates the thiophenol, leaving the other reaction products in solution.



$$\mathrm{RS{-}S{-}\underset{\displaystyle |\atop CH_2{-}COOH}{CH}{-}COOH} + 3OH^- \longrightarrow RS^- + \mathrm{HOS{-}\underset{\displaystyle |\atop CH_2{-}COO^-}{CH}{-}COO^-} + 2\,H_2O \qquad (5)$$

The general procedure, described below, was used to prepare 2,4-dinitrothiophenol, m.p. 128–130°, in 95% yield; 2-nitrothiophenol, m.p. 56°, in 50% yield (with alkali) and in 85% yield (with cyanide as nucleophile); 4-chloro-2-nitrothiophenol, m.p. 122°, in 60% yield; and pentachlorothiophenol, m.p. 232–233°, in 55% yield. The yields are based on the amount of sulfenyl chloride used.

It is, of course, recognized that the required sulfenyl chlorides can, themselves, often best be prepared from thiophenols,[5] so that the conversion ArSCl → ArSH is not always important for synthetic use; and, of course, other routes to the thiophenols listed are available.[6] Nevertheless, the present method is quite convenient, especially when stocks of the stable intermediate disulfides are available, for preparing—as required—quantities of reactive thiols. For example, 2,4-dinitrothiophenol is frequently desired as a reagent for characterizing halides,[7] and it is convenient to prepare it in small amounts, as described above, because of its great tendency to oxidize to the very insoluble disulfide, if not stored quite properly.

The mechanistic factors involved in nucleophilic scission of unsymmetrical disulfides have been discussed at some length in ref. (4). It may be noted that the yields of thiophenols (RSH) recorded agree with the expected effect of electron withdrawing substituents in R on the relative affinities of RS^- and B^- for sulfur (Equation 2), and, hence, on the ease of displacement of RS^-.

EXPERIMENTAL

General procedure. The sulfenyl chloride RSCl (0.1 mole) was dissolved in 100 ml. dry acetic and 0.1 mole of thiomalic acid, suspended in 50 ml. acetic acid, was added, with stirring. The solution was warmed to 70–80° for a few minutes and the acetic acid then removed under reduced pressure to yield the crude disulfide of Equation 4. Without further purification, the thiol was displaced from the above disulfide, by adding an excess of the appropriate nucleophile, as described below.

(a) *Displacement by alkali.* The solid residue was dissolved in 100 ml. 4*N* alkali and refluxed, preferably under nitrogen, for 30 min. The reaction mixture was filtered, cooled, the filtrate acidified with hydrochloric acid and the precipitated thiol collected immediately and recrystallized from ligroin. Thorough drying, and storage under nitrogen, permits the thiols to be stored for long periods without oxidation to disulfide. If considerably stronger alkali is used for the displacement, refluxing is not necessary and a purer product results on acidification. It is probable that some redox reactions of the nitrothiophenoxide ions can occur on heating.

(b) *Displacement by cyanide.* The disulfide obtained by reaction of the sulfenyl chloride and thiomalic acid, by the general procedure above, was dissolved in dilute alkali and 0.1 mole of solid sodium cyanide was added. The reaction mixture was warmed for a few minutes, filtered, and the filtrate acidified (CAUTION: HCN) with hydrochloric acid. The precipitated thiol was purified as described above.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
UNIVERSITY PARK
LOS ANGELES 7, CALIF.

A Vinyl Azlactone

JOHN W. LYNN

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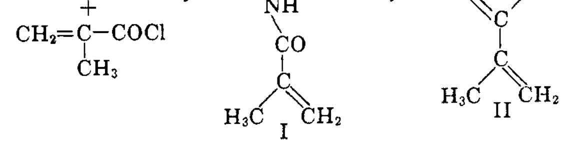
A novel vinyl-polymerizable azlactone, 2-isopropenyl-4-isopropyl-2-oxazolin-5-one (II), was prepared by the cyclodehydration of 2-methacrylamido-3-methylbutyric acid (I), which was prepared by acylation of *dl*-valine with methacrylyl chloride.



Both in homopolymerization and in copolymerization with vinylidene chloride II proved to be a very reactive vinyl monomer. Copolymers of II possess a pendant azlactone group which may provide a site for crosslinking or chemical modification of a resin.

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EXPERIMENTAL[1]

2-Methacrylamido-3-methylbutyric acid (I). A mixture of 117 g. (1 mole) of *dl*-valine (Dow), 400 ml. of water and 80 g. (2 moles) of sodium hydroxide was stirred at 10–15° and 105 g. (1 mole) of methacrylyl chloride (Monomer and Polymer Co.) was added over a 1.5-hour period. The mixture was then treated with 1 mole of concentrated hydrochloric acid. The voluminous precipitate, which formed on standing, was removed by filtration, washed with water, and then recrystallized from benzene to give 141 g., a 75% yield, of I (m.p. 99–100°).

Anal. Calcd. for $C_9H_{15}NO_3$: C, 58.4; H, 8.10; N, 7.56. Found: C, 58.36; H, 8.08; N, 7.65.

2-Isopropenyl-4-isopropyl-2-oxazolin-5-one (II). The technique of Cleaver and Pratt[2] was employed for this closure. A mixture of 18.5 g. (0.1 mole) of I and 51 g. (0.5 mole) of acetic anhydride was added rapidly to 51 g. (0.5 mole) of acetic anhydride at 100°. The mixture was held at 100° for 10 min. and then distilled to give 6.8 g., a 40.5% yield, of II (b.p. 81°/10.5 mm., n_D^{30} 1.4550).

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.78; N, 8.38. Found: C, 64.25; H, 7.68; N, 8.21.

RESEARCH DEPARTMENT
UNION CARBIDE CHEMICALS COMPANY
SOUTH CHARLESTON, W. VA.

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(1) All temperatures are uncorrected.

(2) C. S. Cleaver and B. C. Pratt, *J. Am. Chem. Soc.*, **77**, 1544 (1955).

Some Dimethylaminomethyl Derivatives of Polycyclic Aromatic Hydrocarbons

E. MARCUS AND J. T. FITZPATRICK

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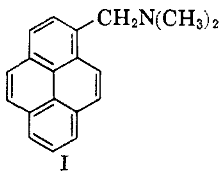
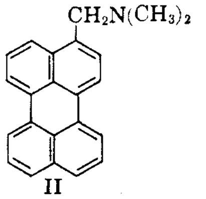
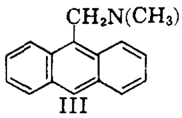
The preparation of dialkylaminomethylbenzenes from aromatic aldehydes and dialkylformamides by the Leuckart reaction has been described previously.[1] We wish to report the extension of the Leuckart reaction to the synthesis of the dimethylaminomethyl derivatives of pyrene, perylene, anthracene, and naphthacene (I–IV).



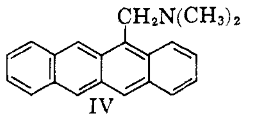
I



II



III



IV

The corresponding aldehydes can be obtained readily by formylation of the hydrocarbons with *N*-methylformanilide or dimethylformamide and phosphorus oxychloride. Refluxing a solution of the aldehyde in dimethylformamide in the presence of formic acid gave fair to good yields of the desired compounds. When the reaction of pyrenecarboxaldehyde with dimethylformamide was carried out in the absence of formic acid, no product at all was obtained. The compounds were isolated as their hydrochlorides.

An alternative route *via* the corresponding chloromethyl derivatives is less satisfactory, because direct chloromethylation of such highly active polycyclic hydrocarbons often leads to diarylmethane-type compounds and bis(chloromethyl) derivatives.[2] When 9-(chloromethyl)anthracene was needed as an intermediate in some recent work, it was made by a three-step synthesis.[3]

EXPERIMENTAL

All melting points are uncorrected. The neutralization equivalents of the amine hydrochlorides were determined by titration with sodium hydroxide using phenolphthalein as indicator; the values are estimated to be accurate within 2 or 3%.

The aldehydes were prepared according to methods described in the literature.[4–7] The melting point of crude 5-naphthacenecarboxaldehyde (m.p. 157–161°) agreed better with the data for analytically pure material reported by Buu-Hoï and Lavit[8] (m.p. 164°) than by Martynoff[7] (m.p 148°). Buu-Hoï and Eckert[9] reported they could use dimethylformamide in place of *N*-methylformanilide for the preparation of 1-pyrenecarboxaldehyde. We found that a fair yield of 1-pyrenecarboxaldehyde could be obtained with dimethylformamide by heating the reaction mixture for 3 hr. at 105°.

As an example for the synthesis of the amines the preparation of *N,N*-dimethyl-1-pyrenemethylamine hydrochloride is described. The hydrochlorides of *N,N*-dimethyl-3-perylenemethylamine, *N,N*-dimethyl-9-anthracenemethylamine, and *N,N*-dimethyl-5-naphthacenemethylamine were made in a similar fashion (Table I).

N,N-Dimethyl-1-pyrenemethylamine hydrochloride. A mixture of 11.5 g. (0.05 mole) of 1-pyrenecarboxaldehyde, 27.5 g. (0.38 mole) of dimethylformamide, and 2.5 ml. of 90% formic acid was refluxed for 4 hr. at about 150°. After removal of the excess of dimethylformamide and formic acid by distillation the residual oil was dissolved in ethyl ether, dried over sodium sulfate, and filtered. Introduction of gaseous hydrogen chloride into the ethereal solution pre-

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