100 cc. of nitrogen gas and 50 cc. of benzene solutions containing about 0.5% of either pale crepe rubber or balata. After sealing, these tubes and a benzene control were exposed to direct sunlight during the summer for various lengths of time up to five weeks. At the end of the tests the changes in volume of the nitrogen in the tubes containing the rubber solutions differed from that of the benzene control by a maximum of 0.5 cc. which was found to be about the limit of experimental error.

Another series of experiments was carried out in an apparatus which consisted of several volumetric reaction chambers in the form of glass tubes fitted with stopcocks and attached to a mercury leveling bulb. The tubes were charged with about 100 cc. of nitrogen and one, reserved for a control, with 50 cc. of pure benzene and the others with 50 cc. each of 1.1% benzene solutions of one of the following types of rubber: pale crepe (from a shipment just received), fine Para from South America, smoked sheet or balata. Even though the tubes were exposed to direct sunlight for three months during the summer the slight changes in volume of the gas were in every case less than 1 cc. and, in each of the rubber solutions, were actual *increases*.

It may be concluded that under the conditions described and with the specimens of rubber, nitrogen and benzene used, nitrogen gas is not absorbed to any appreciable extent.

CONTRIBUTION FROM
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The Formation of Atacamite by the Incorporation of Copper Powder in Magnesium Oxychloride Compositions

BY DEAN S. HUBBELL[1]

When magnesium oxychloride compositions that contain copper harden in the presence of air, the formation of a new phase is indicated by the development of a blue-green color as well as by an increase in strength and a reduction in solubility.

The new blue-green phase was found by X-ray examinations to be identical with atacamite and also cupric oxychloride prepared by dissolving freshly precipitated cupric carbonate in a solution of cupric chloride. This is in harmony with the observations of other investigators[2] who have shown that copper is corroded by certain chloride solutions in the presence of air to form a basic chloride resembling atacamite.

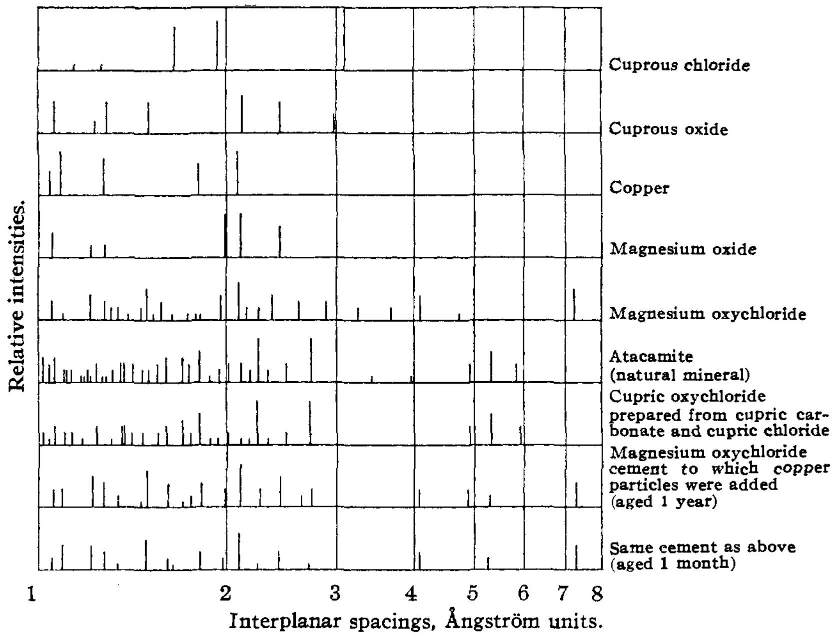

Fig. 1.—Diffraction data.

X-Ray diffraction analyses were made by the Debye–Scherrer method on a sample of the oxychloride cement after aging first for one month and then for one year. The radiation from an X-ray tube provided with a copper target was used, after filtering through nickel, in a camera of 57.3-mm. effective diameter. The specimens used were rods of 0.7-mm. diameter formed from the powdered samples with collodion as a binder. The interplanar spacings obtained from the photograms are shown in the accompanying figure, which includes data obtained in a similar way for cupric oxychloride, atacamite, magnesium oxychloride, copper, cupric chloride, cuprous chloride and magnesium oxide. The relative intensities of the corresponding diffraction lines were estimated visually.

Both unaged and aged oxychloride cements contain, as a major constituent, a material corresponding to magnesium oxychloride, as the similarity of the diffraction data indicates. Diffraction lines corresponding to the stronger

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[2] Benough and May, *J. Inst. Metals*, **32**, 131 (1924); Vernon and Whitby, *ibid.*, **34**, 389 (1930); Mellor, "Inorganic and Theoretical Chemistry," Vol. III, pp. 15, 69, 77, 150, 161; Rooksby and Churnside, *J. Soc. Chem. Ind., Trans.*, **53**, 33 (1934).

lines of cupric oxychloride, and of atacamite, but noticeably broad, were found for these cements, indicating that cupric oxychloride had been formed in appreciable amounts, but in very small, almost colloidal, particles. The amount of this compound is probably somewhat greater in the aged cement than in the unaged material. On the other hand, it is evident that cupric oxychloride has not formed a complex compound with magnesium oxychloride nor entered appreciably into solid solution in it.

It has been observed that the formation of the new phase takes place at the expense of the copper particles and that it cannot proceed in the absence of oxygen or of water vapor. Exposure to sunlight appears to retard and strong ultraviolet light prevents its formation.

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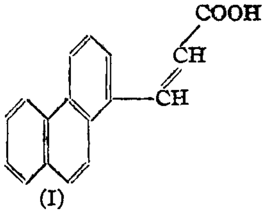
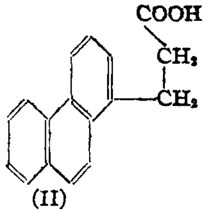
Rapid Synthesis of β-(1-Phenanthryl)-propionic Acid

BY SAMUEL NATELSON AND SIDNEY P. GOTTFRIED

1-Phenanthraldehyde, prepared by the method of Bachmann,[1] was converted rapidly in good yield to β-(1-phenanthryl)-propionic acid after the method described by the authors for a similar series.[2] 1-Phenanthraldehyde, which condenses with acetic anhydride and sodium acetate in extremely poor yield after the usual Perkin reaction, condenses almost quantitatively with malonic acid, with the elimination of carbon dioxide. The β-(1-phenanthryl)-acrylic acid formed (I) may be reduced to yield β-(1-phenanthryl)-propionic acid (II).[3] This acid has been prepared before by Bachmann[1] by a more tedious route in an attempt to synthesize 3′-keto-1,2-cyclopentenophenanthrene.


(I)


(II)

Ten grams of 1-phenanthraldehyde is mixed with 4 g. of malonic acid (excess) and 0.5 cc. of pyridine. The mixture is heated on a water-bath for thirty minutes, when effervescence ceases and the whole mass solidifies. The β-(1-phenanthryl)-acrylic acid, formed in almost quantitative yield, is washed with dilute acid to remove the pyridine and is recrystallized from acetone, m. p. 259°. This acid dissolved in dilute potassium hydroxide, is reduced with an excess of 3% sodium amalgam to yield 9–11 g. of β-(1-phenanthryl)-propionic acid (II), m. p. 187–188° (from acetone). It seems curious to the authors that reduction at the 9,10-positions of the phenanthrene nucleus was not brought about by the sodium amalgam.

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[1] Bachmann, THIS JOURNAL, **57**, 1383 (1935); **58**, 2097 (1936).

[2] Natelson and Gottfried, *ibid.*, **58**, 1432 (1936).

[3] In a private communication, the authors have been informed by Bachmann that he corroborates these observations and has also successfully applied this series of reactions to several phenanthryl aldehydes.

COMMUNICATION TO THE EDITOR

SYNTHETIC VITAMIN B_1

Sir:

In our last communication [THIS JOURNAL, **58**, 1504 (1936)] we reported synthetic vitamin B_1 chloride melting at 232–234° rather than at 246–250° as previously given for the natural product. We have, however, using our previous method but by a different choice of solvents for purification, obtained, in good yield, synthetic vitamin B_1 chloride which agrees in every particular with the natural vitamin. We owe thanks to Dr. G. A. Stein of the Merck Laboratories for his collaboration in this matter.

A low melting point has also been observed in the bromide. In both chloride and bromide the low melting point is associated with a much greater solubility in alcoholic solvents. Both low melting salts are obtained from methanol solutions by addition of ether. However, when recrystallized from methanol by addition of ethanol or from water by addition of ethanol, the higher melting forms have been obtained. The discrepancies in melting