tenophenanthrene from 2-[β-halopropionyl]-phenanthrene were unsuccessful.

3. Diels' hydrocarbon and its ethyl and isopropyl homologs were prepared from the corresponding 2-acylphenanthrene derivatives.

4. Several intermediates and derivatives of the above compounds are described.

EVANSTON, ILLINOIS RECEIVED JUNE 2, 1943

NOTES

Crystalline Bisulfite Addition Compounds of Menadione

BY F. ABLONDI, R. W. PRICE, B R. BAKER AND G. H. CARLSON

Although Moore[1] stated that addition compounds of 2-methyl-1,4-naphthoquinone formed with metallic and amine bisulfites failed to crystallize, the alkali metal,[2] ammonium and calcium derivatives crystallized under the conditions herewith reported. The salts showed antihemorrhagic activity at a concentration of one microgram per milliliter and were convertible to the S-benzylthiuronium salt already described.[2b]

Experimental

Lithium Salt.—Lithium carbonate (15 g.), suspended in 50 cc. of water at 0°, was treated with sulfur dioxide until effervescence ceased, the solution was shaken with 17.4 g. of 2-methyl-1,4-naphthoquinone, insoluble material was filtered off and the filtrate, diluted to 100 cc. and cooled to 5°, yielded 6 g. of crystalline product which, recrystallized from 6 cc. of water, gave the lithium salt. *Anal.* Calcd. for $C_{11}H_9O_5SLi$: Li, 2.68. Found: Li, (1) 3.29; (2) 2.10.

The salt was obtained in better yield by concentrating the filtered bisulfite solution (prepared from 21.5 g. of lithium carbonate, 1 liter water, 100 g. of quinone and sulfur dioxide) *in vacuo* until solid separated and, after fifteen hours at 0°, 84 g. of product was filtered off which, recrystallized from 60 cc. of water and 250 cc. of isopropanol, gave 42 g. of the pure salt. *Anal.* Calcd. for $C_{11}H_9O_5SLi$: Li, 2.68. Found: Li, 2.91.

Ammonium Salt.—Sulfur dioxide was bubbled into 100 cc. of 28% aqueous ammonia at 5° until fumes were no longer evolved, solid deposited at 0° was filtered off, the clarified solution was shaken at 30° with 17.4 g. of the quinone, undissolved solid was filtered off, the filtrate was concentrated *in vacuo* (bath temperature 50°) to a volume of 75 cc. and the crystalline product (4.5 g.), after recrystallization from 3 cc. of water, yielded the pure salt. *Anal.* Calcd. for $C_{11}H_{13}NO_5S$: N, 5.17. Found: N (1), 5.26; (2) 5.10.

Calcium Salt.—A mixture of the quinone (17.4 g.) and a solution prepared by the action of sulfur dioxide upon a suspension of 3 g. of calcium carbonate in 150 cc. of water was stirred 18 hours in an atmosphere of sulfur dioxide, undissolved solid (0.5 g.) was filtered off and the filtrate was evaporated to dryness *in vacuo* (bath temperature 35–40°). The residue was dissolved in 25 cc. of methanol, 75 cc. of isopropanol was added, the filtered solution was concentrated *in vacuo* until the bisulfite compound separated and the product (9.4 g.) was washed with isopropanol. The air-dried salt sintered and melted at 97–98°, the anhydrous at 115–117° (with decomposition). *Anal.* Calcd. for $C_{22}H_{18}O_{10}S_2Ca$: Ca, 7.33. Found: Ca, 7.29.

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(1) Moore, THIS JOURNAL, **63**, 2050 (1941).

(2) The crystalline sodium and potassium salts have already been described: (a) Baker, Davies, McElroy and Carlson, *ibid.*, **64**, 1096 (1942); (b) Menotti, *ibid.*, **65**, 1209 (1943).

4,4'-Dicyanobenzaldazine

BY H. J. BARBER AND R. SLACK

In view of continued interest in 4,4'-diamidinostilbene (Stilbamidine), which is finding increasing use for the treatment of Kala-Azar in India[1] and the Sudan,[2] it was considered necessary to investigate the results claimed by Sah,[3] *viz.*, that 4,4'-dicyanostilbene, an intermediate necessary for the production of the drug, could be obtained by thermal decomposition of the corresponding azine. We had already attempted this unsuccessfully in our work on this product,[4] which is most conveniently prepared from 4,4',α,β-tetrabromodiphenylethane by the action of cuprous cyanide in pyridine.[5]

In no point of detail could his results be confirmed. Three different specimens of *p*-cyanobenzaldehyde (prepared in excellent yield from *p*-

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(1) L. E. Napier, P. C. Sen Gupta and G. M. Sen, *Indian Med. Gaz.*, **77**, 321 (1942).

(2) R. Kirk and M. H. Sati, *Ann. Trop. Med. Parasitol.*, **34**, 83 (1940).

(3) Shou-Cheng Fu and P. P. T. Sah, THIS JOURNAL, **64**, 1482 (1942).

(4) S. Bance, H. J. Barber and A. M. Woolman, *J. Chem. Soc.*, 1 (1943).

(5) British Patent 543,204.

cyanobenzylalcohol by oxidation with nitrogen tetroxide[6,7]) gave, on treatment in alcoholic solution with hydrazine hydrate (50% by wt.), an immediate pale-yellow, microcrystalline precipitate exhibiting the physical properties which might be expected of 4,4'-dicyanobenzaldazine. This product was obtained in almost the theoretical yield, being virtually insoluble in hot alcohol; after crystallization from pyridine or nitrobenzene, from which it separates in yellow needles or plates, it melted at 318–320° (uncor.).

The analyses for nitrogen (Dumas) were consistently slightly low on various samples, but there is little doubt as to the identity of the compound. Calcd. for $C_{16}H_{10}N_4$: C, 74.1; H, 3.75; N, 21.70. Found: C, 74.4; H, 3.88; N, 21.2, 21.5, 21.2, 21.1, 21.2.

Sah describes the azine as being readily soluble in alcohol and having m. p. 118–120°.

Sublimation of our product *in vacuo* (0.5 mm.) resulted in its recovery unchanged but repeated sublimation under normal pressure at 300–320° gave colorless long needles and plates in small yield. Some charring and decomposition to the original aldehyde also occurred at this temperature. Crystallization of the sublimate from glacial acetic acid or nitrobenzene gave slender colorless needles, m. p. 220–223° (uncor.). The melting point of terephthalonitrile[8] was not depressed by this compound.

Although the nature of this decomposition is not clearly understood, there seems little doubt that the compound described is indeed 4,4'-dicyanobenzaldazine: hence, the identity of the product described by Sah is obscure. The possibility of dimorphism cannot be neglected, but a more likely explanation is that the *p*-cyanobenzaldehyde used was impure. It has already been shown in these laboratories that the product obtained from *p*-cyanobenzyl chloride and copper nitrate solution[9,10] is unsatisfactory, being, in fact, a mixture of aldehyde, alcohol and acid.

In this case it is conceivable that other compounds may be isolated (*e. g.*, hydrazine salts), but neither theory explains satisfactorily the production of dicyanostilbene as claimed by Sah.

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[6] Cohen, *J. Chem. Soc.*, 1050 (1897).

[7] J. N. Ashley, *et al.*, *ibid.*, 103 (1942).

[8] British Patent 488,642.

[9] Reinglass, *Ber.*, **24**, 2421 (1891).

[10] Moses, *ibid.*, **33**, 2624 (1900).

A New Form of Crystalline Xylitol

BY J. F. CARSON, S. W. WAISBROT AND F. T. JONES

Wolfrom and Kohn[1] recently succeeded in preparing a hygroscopic crystalline xylitol, m. p. 61–61.5°, by prolonged standing of the sirup in an ice box. In repeating their preparation of this substance from *D*-xylose, the clear viscous sirup which we obtained after concentration *in vacuo*, solidified to a hard, crystalline mass on standing overnight. Recrystallization from either methanol or ethanol yielded colorless crystals melting at 93–94.5°.

From a sample of fused xylitol either type of crystal could be obtained by seeding with the proper nuclei, but the low-melting form, kindly furnished us by Professor Wolfrom, changed in a few days into the high-melting and stable form on exposure to the air of the laboratory.

The low-melting, metastable xylitol separates from alcoholic solution as colorless, lath-shaped crystals with oblique ends similar in appearance to gypsum crystals and is hygroscopic.

The new, high-melting, stable xylitol crystallizes usually as colorless tablets about twice as long as they are wide with symmetrically pointed ends. It is further differentiated from the low-melting form by its ease of crystallization in good yield from methanol, ethanol and even aqueous solution, and by its non-hygroscopic character. Its solubilities at 25° in absolute methanol and ethanol, and in water are, respectively, 6.0, 1.2 and 64.2 g. per 100 g. of solution.

Its identity as anhydrous xylitol was established by the analytical data. *Anal.* Calcd. for $C_5H_{12}O_5$: C, 39.47; H, 7.95. Found: C, 39.52; H, 8.09.

Its identity was further confirmed by conversion to the known pentaacetate.[2] Colorless plates, m. p. 63–64°, were obtained which showed no depression when mixed with an authentic specimen of xylitol pentaacetate, m. p. 62.5–63.5°.

Crystallographic Analysis of Two Crystalline Forms of Xylitol.—The two crystalline modifications were examined under a petrographic microscope, and refractive indices were determined with monochromatic sodium light by the immersion method. The orientation in each case was verified by means of interference figures. The crystallographic properties of the two crystalline forms of xylitol are given in Table I.

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[1] Wolfrom and Kohn, THIS JOURNAL, **64**, 1739 (1942).

[2] R. C. Hockett and C. S. Hudson, *ibid.*, **57**, 1753 (1935).