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.

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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.[2a]

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.

LEDERLE LABORATORIES
PEARL RIVER, N. Y. RECEIVED JULY 8, 1943

(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**, 1200 (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*-

(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.