no trace of excess C^{13} was found in the carboxyl group of the phenylacetic acid.

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

RECEIVED MAY 23, 1946

Thio-Michler Ketone and bis-(Dimethylaminopyridyl)-thioketone[1]

BY D. S. TARBELL AND V. P. WYSTRACH[2]

It became necessary to prepare considerable amounts of thio-Michler ketone (bis-(4-dimethylaminophenyl)-thioketone) and related compounds, having an electron-donating group in the para position to the thioketone function. The method described below, which is a modification of Graebe's synthesis,[3] was found to be by far the most convenient procedure of several that were tried for thio-Michler ketone.

The action of sulfur at 190° on bis-(2-dimethylamino-5-pyridyl)-methane has been reported[4] to yield the corresponding thioketone, bis-(2-dimethylamino-5-pyridyl)-thioketone, melting at 196° with decomposition. He obtained by the same procedure a compound melting at 166–168° without decomposition, and, since only a sulfur analysis had been reported by Tchitschibabin,[4] we had our sample analyzed for carbon and hydrogen. The result agreed with the thioketone structure for the compound; apparently the thioketone is either dimorphic or the previously[4] reported melting point is in error.[5]

Experimental

Thio-Michler Ketone.—One hundred grams (0.33 mole) of auramine (4,4'-dimethylaminobenzophenone imide hydrochloride) was dissolved in 850 cc. of alcohol on the steam-bath. The solution was cooled to room temperature, and a fairly rapid stream of ammonia gas was bubbled in until the crystals of auramine had gone into solution (ten to fifteen minutes). Hydrogen sulfide gas was bubbled in for fifteen minutes at room temperature and then for thirty minutes at the boiling point of the solution. The thioketone began to crystallize out at this point. The reaction mixture was cooled in an ice-bath, and the deep red-violet crystals collected and washed with two 150-cc. portions of methanol. The rather crude product usually amounted to 61.0–62.3 g. and melted at 193–200°.

The crude material was placed in a large Soxhlet extractor and extracted with 500 cc. of chloroform. After the extraction was complete, about half of the solvent was allowed to distill up into the extractor and the process was interrupted at this point. This procedure left the proper amount of solvent in the flask for recrystallization. Methanol (500 cc.) was then added slowly to the chloroform solution of the thioketone, and the mixture boiled for a few minutes. After standing overnight in the ice box, the deep purple crystals were collected by filtration and washed with two 150-cc. portions of cold methanol. The yield by this procedure was 41.5–44.1 g. (56–59%), m. p. 202–204°.

***bis*-(2-Dimethylamino-5-pyridyl)-thioketone.**—This product was prepared in very poor yield from the corresponding dipyridylmethane and sulfur,[4] and melted at 166–168°.

Anal.[6] Calcd. for $C_{15}H_{18}N_4S$: C, 62.91; H, 6.33. Found: C, 62.89; H, 6.31.

---

[1] The work done in this note was carried out under a contract, recommended by the National Defense Research Committee, between the Office of Scientific Research and Development and the University of Rochester. The National Defense Research Committee assumes no responsibility for the accuracy of statements contained in this note.

[2] Present address: American Cyanamid Company, Stamford, Connecticut.

[3] Graebe, *Ber.*, **20**, 3267 (1887); other procedures are given by Wallach, *Ann.*, **259**, 303 (1890); Fehrmann, *Ber.*, **20**, 2857 (1887); Baither, *ibid.*, **20**, 3289 (1887); Reddelien and Danilof, *ibid.*, **54**, 3132 (1921).

[4] Tchitschibabin and Knunjanz, *ibid.*, **62**, 3048 (1929).

[5] In a paper published after our work was complete, Kahn and Petrow, *J. Chem. Soc.*, 858 (1945), reported an improved method for the preparation of bis-(2-dimethylamino-5-pyridyl)-thioketone, using the dipyridylmethane and sulfur in pseudocumene solution. They did not give the melting point of the product.

[6] Analysis by Dr. Carl Tiedcke.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

RECEIVED JUNE 25, 1946

Acetylation of D-Mannose Phenylhydrazone

BY M. L. WOLFROM AND MARY GRACE BLAIR[1]

Crystalline pentaacetates of D-glucose phenylhydrazone[2] and D-galactose phenylhydrazone[3,4] are known; tetraacetates of D-glucose phenylosazone[5,6,7] and D-galactose phenylosazone[7] have been synthesized; and the pentaacetates of the enantiomorphous and racemic forms of galaheptose phenylosazone[8] have been reported. On extending the mild acetylation conditions employed by Wolfrom, Konigsberg, Soltzberg and Georges[7] to D-mannose phenylhydrazone, a crystalline product was obtained that was characterized by analysis as the O-tetraacetate of an anhydride of a hexose phenylhydrazone. It is thus established that the phenylhydrazone of D-mannose undergoes anhydride formation with great ease. Such a reaction has hitherto been obtained with sugar osazones and then only by acetylation followed by alkaline deacetylation[9] or by acid treatment.[10] Percival[11] has presented evidence against the pyrazoline structure suggested for these substances by Diels and co-workers.[12] While no definitive structure for the presently described product may be established on the evidence now available, the apparent presence of four O-acetyl groups would favor a pyrazoline structure (I).

---

[1] Sugar Research Foundation Fellow of The Ohio State University Research Foundation (Project 190).

[2] A. Hofmann, *Ann.*, **366**, 277 (1909).

[3] M. L. Wolfrom and C. C. Christman, THIS JOURNAL, **53**, 3413 (1931).

[4] J. Compton and M. L. Wolfrom, *ibid.*, **56**, 1157 (1934).

[5] L. L. Engel, *ibid.*, **57**, 2419 (1935).

[6] K. Maurer and B. Schiedt, *Ber.*, **68B**, 2187 (1935).

[7] M. L. Wolfrom, M. Konigsberg, S. Soltzberg (and L. W. Georges), THIS JOURNAL, **58**, 490 (1936).

[8] R. M. Hann and C. S. Hudson, *ibid.*, **61**, 336 (1939).

[9] E. G. V. Percival, *J. Chem. Soc.*, 1770 (1936); E. E. Percival and E. G. V. Percival, *ibid.*, 1320 (1937).

[10] E. Fischer, *Ber.*, **20**, 821 (1887); O. Diels and R. Meyer, *Ann.*, **519**, 157 (1935).

[11] E. G. V. Percival, *J. Chem. Soc.*, 783 (1945).

[12] O. Diels, R. Meyer and O. Onnen, *Ann.*, **525**, 94 (1936).