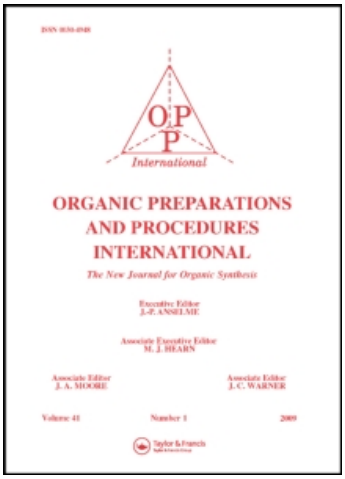


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

2,3,6-TRI(ACETOXYMERCURI)-4-(TRIMETHYLAMMONIUM)ANILINIUM DIACETATE BY DIRECT TRIACETOXYMERCURATION

H. A. Friedman[a]; G. B. Koelle[a]
[a] Department of Pharmacology, University of Pennsylvania School of Medicine, Philadelphia, Pennsylvania

To cite this Article Friedman, H. A. and Koelle, G. B.(1973) '2,3,6-TRI(ACETOXYMERCURI)-4-(TRIMETHYLAMMONIUM)ANILINIUM DIACETATE BY DIRECT TRIACETOXYMERCURATION', Organic Preparations and Procedures International, 5: 5, 251 — 253
To link to this Article: DOI: 10.1080/00304947309356850
URL: http://dx.doi.org/10.1080/00304947309356850

ORGANIC PREPARATIONS AND PROCEDURES, INT. 5(5), 251-253 (1973)

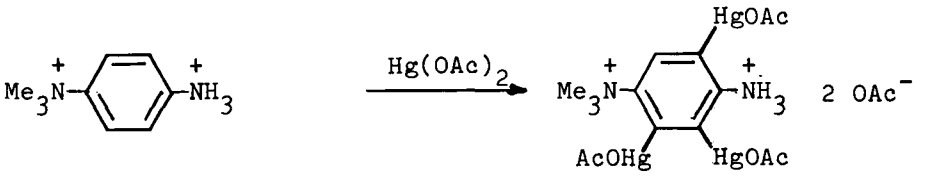
2,3,6-TRI(ACETOXYMERCURI)-4-(TRIMETHYLAMMONIUM)ANILINIUM DIACETATE BY DIRECT TRIACETOXYMERCURATION

H. A. Friedman* and G. B. Koelle

Department of Pharmacology, University of Pennsylvania
School of Medicine, Philadelphia, Pennsylvania 19174

Aromatic amines readily undergo mercuration reactions with mercuric acetate to give substituted mercurated compounds, in accordance with the general laws of substitution in amines. Thus, monosubstituted o- and p-mercurated derivatives may be obtained from aniline.[1,2] An excess of mercuric acetate will give the 2,4-dimercurated product.[3] Mercuric sulfate has been reported to yield the trimercurated derivative.[4]

We now report a very facile and direct preparation of 2,3,6-tri(acetoxymercuri)-4-(trimethylammonium)anilinium diacetate; even when the reaction was run with only two equivalents of mercuric acetate, only the trimercurated derivative was isolated. The position of the acetoxymercuri groups was assigned on the basis of the o-p directing effect of the amino



group. This synthesis was developed as part of a program for the localization of pharmacological receptor sites by electron microscopy.

EXPERIMENTAL

Trimethyl (p-aminophenyl)ammonium chloride hydrochloride[5] (3.1 g., 0.014 mole) was dissolved in 50 ml. of water. A slurry of silver acetate(4.6 g., 0.028 mole) in 25 ml. of water containing 10 ml. of glacial acetic acid was added to the solution of the amine hydrochloride. The mixture was stirred at room temperature for 1 hr. The colloidal suspension that initially developed precipitated and the original pink color turned to a straw color. It is imperative that the stoichiometry be achieved to as great a degree as possible since an excess of either silver acetate or chloride ion will cause severe complication during the isolation of the product. The silver chloride formed was removed by filtration and a solution of mercuric acetate (13.3 g., 0.042 mole) in 50 ml. of water was added to the filtrate. The solution was heated under reflux for 2 hrs. until the initial deep red color turned yellow. After removal of the water *in vacuo*, ethanol was added and the mixture evaporated *in vacuo* to yield a syrup. Repetition of this procedure caused the product to crystallize. The precipitate was collected and washed with absolute ethanol to yield 11.4 g.(78%) of product. One recrystallization from 95% ethanol afforded 8.6 g.(57%) of pure material. An analytical sample was obtained by two additional crystallizations from 95% ethanol; the compound underwent decomposition without melting, beginning at about 130°.

Anal. Calcd for $C_{19}H_{28}N_2O_{10}Hg \cdot 1/4C_2H_5OH$: C, 22.14; H, 2.81; N, 2.64; Hg, 56.78. Found: C, 22.34; H, 2.90; N, 3.14; Hg, 56.84.

NMR(100% D_2O) ppm: 2.01 (15 H, s, CH_3C), 3.59 (9 H, s, Me_3N^+), 4.70 (3 H, s, OH as exchangeable protons), 7.50-7.80 (1 H, aromatic H); the presence of ethanol of crystallization was confirmed by the nmr spectrum; 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt was used as an internal standard.

REFERENCES

1.- O. Dimroth, Ber., 35, 2853 (1902).

2.- A. Piccinini and G. Ruspaggiari, Gazz. Chim. Ital., 22, 604 (1892).

3.- L. Vecchiotti, ibid., 44, 35 (1914).

4.- F. J. Sowa, U. S. Patent 2,607,790 (1952).

5.- P. S. Traylor and S. J. Singer, Biochem., 6, 881 (1967).

Acknoledgement.- The support of this work by Grant No. USPHS 5 R01 NS00282-21 is gratefully acknowledged.

(Received May 29, 1973; in revised form August 16, 1973)