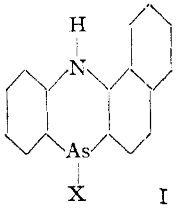
EVIDENCE FOR AN ASYMMETRICAL TRIVALENT ARSENIC ATOM

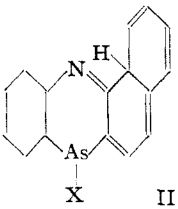
Sir:

The resolution of trivalent nitrogen compounds having three different substituent groups has long baffled organic chemists. Based on certain observations recorded in the literature, it would seem that when a molecule contains a nitrogen atom surrounded by three different groups and a lone pair of electrons, it should be asymmetrical, and capable of resolution if it contains the radicals usually employed for this purpose. Failure to accomplish this has been explained in several ways, one of which is that racemization is so rapid that the optically active molecule has too short a life. Assuming that the presence of additional shells of electrons around the kernel would tend to make a more stable arrangement, a properly constituted trivalent arsenic compound might be capable of resolution, thus showing that such a substance is asymmetrical.

7-Chloro-7,12-dihydro-γ-benzophenarsazine (Formula I, X = Cl) is such a substance. On treatment with silver *d*-bromocamphor sulfonate, dimers (A, B) having different rotations are obtained.



I



II

Subs.	Sp. rot.	Mol. rot.	Calcd. half life, min.	Calcd. sp. rot. for As radical
A	+35.11°	+211.4°	70	−24.68°
B	+59.52°	+358.4°	36	+22.65°

Although the arsenic compound has not yet been regenerated from the camphor complex, the formation of these dimers indicates the presence of two asymmetric centers, one of which is in the camphor residue. Both the arsenic and nitrogen atoms are asymmetrical as represented, but since there is yet no recorded case of optical activity of compounds containing trivalent nitrogen, the activity in this instance is probably due to the arsenic. The existence of an asymmetric carbon atom, formed by a 1,3-shift of hydrogen (Formula II), though not excluded seems improbable.

McGILL UNIVERSITY C. F. H. ALLEN
MONTREAL, CANADA F. B. WELLS

RECEIVED JULY 31, 1933 PUBLISHED SEPTEMBER 5, 1933

ARSENATED DERIVATIVES OF PHENOBARBITAL

Sir:

An investigation of arsenated derivatives of phenobarbital undertaken several years ago in this Laboratory involves the use of 5-nitrophenyl-5-

ethylbarbituric acid and related compounds described by Bousquet and Adams [THIS JOURNAL, **52,** 227 (1930)]. Through the Bart reaction, 5-aminophenyl- and 5-nitroaminophenyl-5-ethylbarbituric acids have been converted into the arsonic acids, 5-arsonophenyl- and 5-nitroarsonophenyl-5-ethylbarbituric acids. By means of hypophosphorous acid the latter were reduced to the corresponding arseno compounds.

During the research it became necessary to establish the position of the nitro group in the starting product and it was shown to be meta. In view of a recent article in this field [Rising, Shroyer and Stieglitz, *ibid.*, **55,** 2819, footnote (1933)] in which mention is made of a forthcoming communication by Rising and Pierce concerning the structure of 5-nitrophenyl-5-ethylbarbituric acid, a brief outline is given here of the method of proof used in our work. 5-Nitrophenyl-5-ethylbarbituric acid (m. p. 279–280°) [all melting points are corrected] ⟶ (nitrophenylethylmalonic acid) ⟶ α-nitrophenylbutyric acid (80% yield, m. p. 115.5–116.3°; neutral equivalent 210, calcd. 209.1) ⟶ *m*-nitrobenzoic acid (60% yield, m. p. 141–142°; identity confirmed by mixed m. p.).

5-*m*-Aminophenyl-5-ethylbarbituric acid was converted to a 5-(nitro-*m*-aminophenyl)-5-ethylbarbituric acid (dec. 330–340°) by the method of Bousquet and Adams, and by elimination of the amino group a new isomeric 5-nitrophenyl-5-ethylbarbituric acid (dec. 327–330°) was obtained. In the latter the nitro group may occupy the ortho or para position; the difficulty of hydrolyzing this compound has prevented us from establishing its structure.

BAKER LABORATORY OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK
MILTON T. BUSH
JOHN R. JOHNSON

RECEIVED AUGUST 2, 1933 PUBLISHED SEPTEMBER 5, 1933

THE NITRATION OF PHENOBARBITAL

Sir:

As stated in a previous publication [THIS JOURNAL, **55,** 2817 (1933)] the authors have proved that the nitration of phenobarbital

$$(C_6H_5)(C_2H_5)\underbrace{CCONHCONHC}=O$$

leads to the formation of 5-*m*-nitrophenyl-5-ethylbarbituric acid.[1,2] That the product of nitration of melting point 279–280° (corr.) is the meta, and not the para, isomer was proved as follows: 8.4 g. of the nitro-ureide yielded on oxidation 1.0 g. of *m*-nitrobenzoic acid, which was identified by

---

(1) In confirmation of the findings of the present authors, Bush and Johnson have recently offered evidence for the formation of the meta rather than the para derivative.

(2) It is of interest to note that the sulfonation of phenobarbital leads to a meta derivative. (Stieglitz and Yoran, unpublished dissertation for the doctorate degree, University of Chicago, June, 1933).