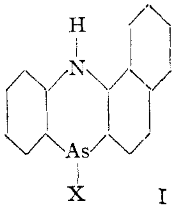
EVIDENCE FOR AN ASYMMETRICAL TRIVALENT ARSENIC ATOM

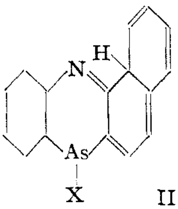
Sir:

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.

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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-