[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

Evidence for an Asymmetrical Arsenic Atom

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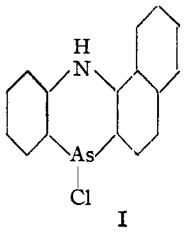
Many ingenious but unsuccessful attempts have been made to resolve suitably constituted derivatives of trivalent nitrogen; the theoretical discussion of this problem has been covered by several authors.[1] If the real reason for the failure to isolate *d* and *l* forms of trivalent nitrogen compounds is their great ease of racemization, then compounds of elements of higher atomic number in Group V of the Periodic Table might be expected to be more stable spatially and resolvable if they contained the necessary groups. On account of its relative insensitiveness to oxidation and reduction, and extensive known chemistry, arsenic was selected for testing.

If trivalent arsenic with three different groups is asymmetrical, the formation of diastereoisomers on treatment of the chloroarsazine (I) with silver *d*-bromocamphor sulfonate would be interpreted as positive evidence of that assumption. When a solution of these substances in acetic anhydride is heated for a few minutes and filtered from silver chloride, two isomeric substances (II, A, B) are obtained and separated by fractional crystallization. These have different rotations. An isomeric chloride (IV), prepared from phenyl-α-naphthylamine and a homolog from *p*-tolyl-α-naphthylamine were also treated in a similar manner; from the latter only one substance (III, formula II,* = CH_3) could be isolated, and the former proved useless for our purpose.



I

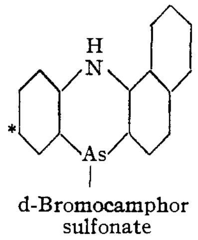
TABLE I

ROTATIONS OF ARSENIC SULFONATES

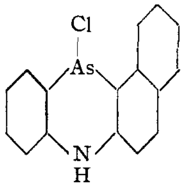
Substance	IIA	IIB	III
Specific rotation	+ 35.1	+ 59.5	+32.6
Molecular rotation	+211.4	+358.4	+200.7
Calcd. mol. rot. of As radical	− 72.1	+ 74.9	− 82.6
Calcd. spec. rot. of As radical	− 24.9	+ 25.6	− 27.0
Calcd. half life,[a] minutes	70	36	25

[a] In the sunlight. The substance has been kept in the dark for a month with no change in rotation.

In the last two columns the values given are calculated for the part of the molecule containing the arsenic—the diastereoisomers have not yet been successfully split to regenerate a chloroarsine.



II



IV

If a tetrahedral structure be assumed for both nitrogen and arsenic, geometrical isomerism is possible, the H and Cl being on the same or opposite sides of the molecule. In this case the two optically active compounds might be derived from the two possible forms. However, since there is as yet no recorded instance of optical activity of compounds containing secondary amino nitrogen, the activity in this case is probably due to the arsenic.

As represented by the octet theory, an arsine would be $R_1:\overset{R_2}{\underset{\cdot\cdot}{\ddot{As}}}:R_3$. The asymmetry of the molecule is then due to three different groups around a central atom, and a lone pair of electrons which acts as the equivalent of a fourth group. Regardless of just how a molecule in space is actually constituted, such a method of representation is of practical value in enabling one to predict types of substances that should be capable of resolution; the essentials are three different groups and a lone pair of electrons around a fourth atom. This conception makes it possible to predict optical activity in many compounds where none would be expected according to the old type or formula, *e. g.*, substances containing trivalent carbon,[2] or the sodium salts of aci-nitro compounds.

At the outset of this work attempts were made to prepare a substance like (V), in which, if the arsenic atom is asymmetrical, there should be two different centers of asymmetry, and two inactive compounds would be expected experi-

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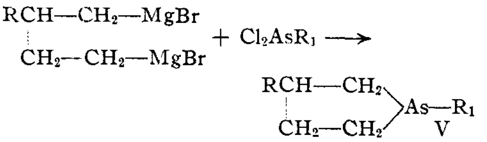
[1] G. Wittig, "Stereochemie"; S. Goldschmidt, "Stereochemie"; Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany; Adams, *Chem. Rev.*, **12**, 323 (1933). Richter, *ibid.*, **10**, 387 (1932); Mills, *Chem. and Ind.*, **51**, 750 (1932).

[2] Wallis and Adams, THIS JOURNAL, **55**, 3838 (1933).

mentally. The reaction for securing cyclic arsenic compounds[3] was already known, but only straight chain halides had been used. This



V

course was blocked because it was not possible to prepare Grignard reagents from branched chain dihalides.[4]

Experimental

The Chloroarsazines.—In the purification of 7-chloro-7,12-dihydro-γ-benzophenarsazine[5] it was found essential to use a solvent that had been dried by refluxing over sodium, and *p*-cymene was preferable to xylene. The yield of pure product was 61%. The isomeric 12-chloro-7,12-dihydro-α-benzophenarsazine (V) was prepared in a similar manner from phenyl-β-naphthylamine; the yield was 70%. It crystallizes in fine yellow rods from cymene, m. p. 252–253°. The 7-chloro-9-methyl-7,12-dihydro-γ-benzophenarsazine (VI) was obtained from *p*-tolyl-α-naphthylamine[6] in a yield of 47%. It formed shiny greenish-yellow prisms, of m. p. 258–259°.

Subs.	Formula	Calcd. Cl	Calcd. As	Found Cl	Found As
V	$C_{16}H_{11}NClAs$	10.8	22.9	10.6	23.1
VI	$C_{17}H_{13}NClAs$	10.4	21.5	10.7	21.7

Reactions with the Silver Salt.—A mixture of 5 g. of the chloroarsazine, an equivalent amount of silver *d*-α-bromocamphor sulfonate and 10 cc. of acetic anhydride was boiled for ten minutes, the silver chloride filtered off and the solvent removed *in vacuo*. The residual brown solid was treated with hot 95% alcohol and fractionally crystallized. The first two solids that separated (m. p. 211–212, 200°) were free from halogen and not investigated. The next yellow powder (II B), m. p. 188–189°, weighed 0.6 g. The fourth substance (II A) formed brown prisms, m. p. 182–183°, 0.25 g. being obtained.

The isomeric 12-chloroarsazine (IV) also gave four substances on a similar treatment, of which the first two were bromine-free. The third (VII) formed yellow prisms, m. p. 224–225° and the fourth (VIII) brown prisms, m. p. 218–219°. The 9-methyl homolog of (I) was more susceptible to decomposition and was only refluxed for five minutes in acetic anhydride. Some unchanged chloroarsazine and much tarry material were the principal products. Only 0.25 g. of the desired compound (III) was isolated; it formed yellow prisms, m. p. 250°.

Subs.	Formula	Calcd. Br	Calcd. As	Found Br	Found As	$(\alpha)^{25}_{D}$
IIA	$C_{26}H_{35}O_4NSBrAs$	13.2	12.4	12.9	12.7	+35.1
IIB	$C_{26}H_{35}O_4NSBrAs$	13.2	12.4	13.0	12.3	+59.5
VII	$C_{26}H_{35}O_4NSBrAs$	13.2	12.4	12.9	12.2	
VIII	$C_{26}H_{35}O_4NSBrAs$	13.2	12.4	13.0	12.7	
III	$C_{27}H_{37}O_4NSBrAs$	13.0	12.2	13.2	12.5	+32.6

The rotations were determined in 95% alcohol, using 0.122 g. per 25 cc. The solution is practically saturated and as deeply colored as can be read conveniently in a 0.5 decimeter tube. The rotation remained constant if the solutions were kept in the dark, but in the light the rotations slowly changed and the solutions became deeply colored. The values of the first two represent the means of twenty readings, while the last was from five. The rotations of (VII) and (VIII) were smaller than the experimental error and so valueless.

Summary

The treatment of 7 - chloro - 7,12 - dihydro - γ - benzophenarsazine with silver *d*-α-bromocamphorsulfonate produced two optically active substances with opposite and approximately equal rotations. The formation and mutarotation of these diastereoisomers may be considered as evidence in favor of an asymmetrical trivalent arsenic atom.

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[3] Grüttner and Wiernik, *Ber.*, **48**, 1473 (1915); Grüttner and Kraus, *ibid.*, **49**, 437 (1916); Steinkopf, Schubart and Roche, *ibid.*, **65**, 409 (1932).

[4] Allen, Wilson and Ball, *Can. J. Res.*, **9**, 432 (1933).

[5] Lewis and Hamilton, This Journal, **43**, 2218 (1921).

[6] Specimens of these amines were kindly supplied by E. I. du Pont de Nemours & Co., Inc., and are gratefully acknowledged.