from ethyl acetate containing some methanol gave 12.1 g. (36%) of product.

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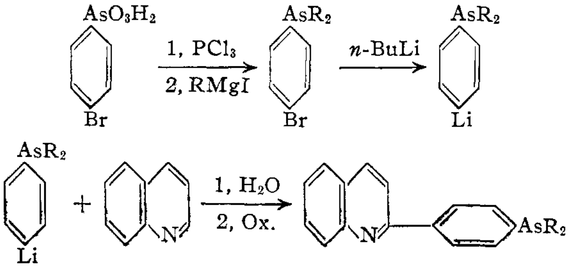
Some Aromatic and Heterocyclic Dialkylarsines

BY HENRY GILMAN AND SOUREN AVAKIAN

RECEIVED MARCH 5, 1954

In connection with studies on the preparation and properties of aromatic and heterocyclic organolithium compounds derived from reactions of metalation and halogen–metal interconversion, it was considered worthwhile to synthesize some selected dialkylarsine types easily derived from the corresponding organometallic compounds. These arsenic containing compounds were of interest primarily for evaluation of their biological activities.

A typical reaction sequence is



A second route for introduction of the dialkylarsino groups involved the coupling of a dialkyliodoarsine with an organometallic compound as

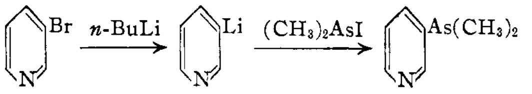


TABLE I

DIALKYLARSINO COMPOUNDS

Compound	M.p., °C.	B.p. °C.	B.p. Mm.	Yield, %	Arsenic, % Calcd.	Arsenic, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
p-Dimethylaminophenyldimethylarsine[a]		136–137	15	73			6.22	6.31
1,4-Bis-(dimethylarsino)-benzene[b]		146–148	16	91	52.41	52.28		
2-Pyridyldimethylarsine		90–91	14	81			7.65	7.72
3-Pyridyldimethylarsine		105–107	16	58			7.65	7.76
p-Bromophenyldiallylarsine[c]		105–106	0.06	73	23.80	23.92		
p-Bromophenyldipropylarsine[d]		106–107	0.05	94	23.64	23.79		
8-Methyl-2-(p-di-n-propylarsinophenyl)-quinoline[e]	84–85			79			3.69	3.76
6-Methoxy-2-(p-di-n-propylarsinophenyl)-quinoline[e]	95–96			76			3.54	3.61

[a] The picrate derivative melts at 159–160°. [b] Prepared from p-dimethylarsinophenylmagnesium bromide and dimethyliodoarsine. [c] Prepared from p-bromophenyldichloroarsine and allylmagnesium bromide. [d] Prepared from p-bromophenyldichloroarsine and n-propylmagnesium bromide. [e] Recrystallized from ethanol.

Experimental[1]

p-Bromophenylarsonic Acid.[2]—A mixture of 34.0 g. (0.2 mole) of p-bromoaniline and 1.5 l. of 1 N hydrochloric acid was diazotized and the resulting solution added slowly with stirring to 7.0 l. of a cold aqueous solution of 30 g. of sodium arsenite, 0.5 g. of copper sulfate and 300 g. of sodium carbonate. Stirring was continued for five hours after which the reaction mixture was allowed to stand at room temperature for 12 hours. Filtration followed by concentration to 1.5 l. and acidification of the filtrate precipitated 45 g. (80%) of p-bromophenylarsonic acid, melting above 310°.

Anal. Calcd. for $C_6H_5AsBrO_3$: As, 26.75. Found: As, 26.92.

p-Bromophenyldichloroarsine.—A solution of 20 ml. of phosphorus trichloride in 30 ml. of acetic acid was added slowly to a suspension of 20.0 g. (0.072 mole) of p-bromophenylarsonic acid in 100 ml. of boiling acetic acid. The mixture was heated under reflux for 30 minutes, cooled and 200 ml. of concentrated hydrochloric acid added. The precipitated oil was separated, dissolved in benzene, washed with water, dried over sodium sulfate and distilled to yield 17 g. (80%), b.p. 90–91° (3.0 mm.).

Anal. Calcd. for $C_6H_4AsBrCl_2$: As, 21.50. Found: As, 21.21.

p-Bromophenyldimethylarsine.—A solution of 54 g. (0.18 mole) of p-bromophenyldichloroarsine in 300 ml. of ether was added slowly with stirring and ice-bath cooling to a solution of 0.46 mole of methylmagnesium iodide in ether. The mixture was stirred for 30 minutes after completion of the addition, hydrolyzed with water and the ether layer separated and dried. Distillation gave 91% of p-bromophenyldimethylarsine boiling at 130–131° (17 mm.), $n^{20}\text{D}$ 1.6105, $d^{20}{}_4$ 1.6082. This compound has been reported by Jones,[3] b.p. 134–136° (9 mm.), and Blicke,[4] b.p. 120–125° (11 mm.).

Anal. Calcd. for $C_8H_{10}AsBr$: As, 28.71. Found: As, 28.82.

p-Carboxyphenyldimethylarsine.—A solution of 13.0 g. (0.05 mole) of p-bromophenyldimethylarsine in 200 ml. of ether was converted to the Grignard reagent with 2.3 g. (0.1 g. atom) of magnesium. Treatment with solid carbon dioxide and work-up in the usual manner gave the carboxylic acid in 80% (9.0 g.) yield. The acid melted at 143–144°.

The compound was also prepared in 63% yield by carbonation of the product of halogen–metal interconversion of n-butyllithium and p-bromophenyldimethylarsine.

Anal. Calcd. for $C_9H_{11}AsO_2$: As, 33.15. Found: As, 33.38.

Dimethyliodoarsine.—This compound was prepared by a combination and modification of the procedures of Wigren[5] and McKenzie.[6] Methyl iodide (350 g.) was added to a solution of 110 g. of arsenious oxide and 194 g. of sodium hydroxide in 2 l. of 80% ethanol in water. After 20 hours the alcohol was removed by distillation, the residue acidified with hydrochloric acid and then saturated with sulfur dioxide. During passage of the sulfur dioxide, 210 g. of sodium iodide was added in small portions. The precipitated methyldiiodoarsine was separated, dissolved in 800 ml. of ethanol and treated with a solution of 208 g. of sodium hydroxide in 300 ml. of water and 85 ml. of methyl iodide. After standing overnight the alcohol was removed by distillation, the residue acidified with hydrochloric acid and saturated with sulfur dioxide. The product was dissolved

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(1) All melting and boiling points are uncorrected.

(2) A. Mouneyrat, English Patent 142,947 (1919) [*C. A.*, **14**, 2802 (1920)].

(3) W. J. Jones, *et al.*, *J. Chem. Soc.*, 2287 (1932).

(4) F. F. Blicke and S. R. Safir, THIS JOURNAL, **63**, 575 (1941).

(5) N. I. Wigren, *Ann.*, **437**, 285 (1924).

(6) A. McKenzie and J. K. Wood, *J. Chem. Soc.*, **117**, 406 (1920).

in ether, washed with water, dried over sodium sulfate, and distilled. The yield of dimethyliodoarsine boiling at 154–155° was 157 g. or 46%.

3-Quinolyldimethylarsine.—A solution of 26.6 g. (0.12 mole) of dimethyliodoarsine in 200 ml. of ether was added with stirring over a 15-minute period to an ether solution of 0.12 mole of 3-quinolyllithium[7] cooled to −15°. The mixture was stirred for one hour after completion of the addition, hydrolyzed and the ether layer separated and dried. Distillation gave 21 g. (74%) of 3-quinolyldimethylarsine boiling 124–127° at 0.5 mm. pressure.

Anal. Calcd. for $C_{11}H_{12}AsN$: N, 6.01. Found: N, 6.18.

2-(Di-*n*-propylarsinophenyl)-quinoline.—*p*-Bromophenyldi-*n*-propylarsine (39 g. or 0.15 mole) was treated with *n*-butyllithium in the usual fashion for halogen–metal interconversion[8] and the resulting solution of *p*-lithiophenyldi-*n*-propylarsine was added with stirring at 0° over a 30-minute period to a solution of 15.3 g. (0.12 mole) of quinoline in 50 ml. of ether. The reaction mixture was hydrolyzed with water and a few ml. of nitrobenzene added for oxidation of the intermediate dihydro compound. Separation of the ether layer followed by drying over sodium sulfate and distillation gave 26 g. (60%) of product boiling at 218–219° (0.08 mm.).

Anal. Calcd. for $C_{21}H_{24}AsN$: N, 3.83. Found: N, 3.78.

The compounds listed in Table I were prepared in general accordance with the procedures described above.

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[7] H. Gilman and S. Spatz, This Journal, **63**, 1553 (1941).

[8] R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y.

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The Anomalous Reduction of 7,9-Diketoperinaphthane and its Methyl Ether

BY MARTIN GOLDMAN[1]

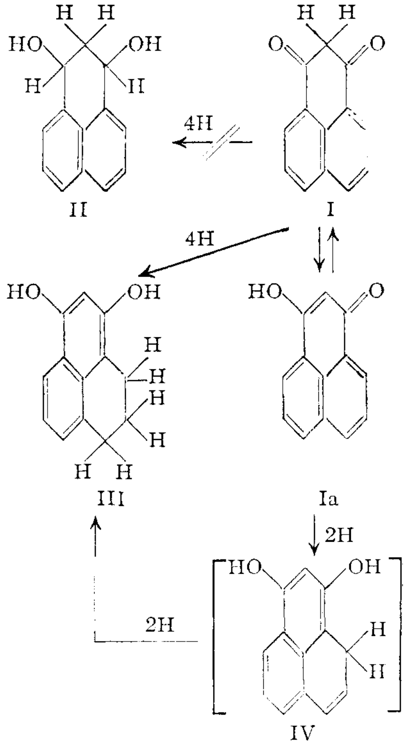
RECEIVED NOVEMBER 25, 1953

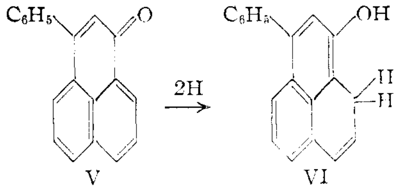
During recent attempts to synthesize bromoperinaphthene,[2] the reduction of 7,9-diketoperinaphthane (I) was investigated for the purpose of preparing 7,9-dihydroxyperinaphthane (II).

However, instead of the desired alcohol, the isomeric phenol, 1,3-dihydroxyperinaphthane (III), was obtained as the product of the reduction.

Several attempts to reduce 7,9-diketoperinaphthane by means of lithium aluminum hydride in ether or in tetrahydrofuran solution were unsuccessful. Similarly, sodium borohydride in aqueous sodium hydroxide appeared to be without action on the diketone. However, Adams catalyst effected the reduction of I in ethanolic solution to the phenol III. Somewhat more unexpected was the fact that the use of Raney nickel catalyst, which does not ordinarily catalyze the reduction of aromatic nuclei under mild conditions,[3] afforded the same compound in a reduction conducted at room temperature and at atmospheric pressure.

This mode of reduction of the diketone was not completely surprising in view of its existence in the tautomeric form of 9-hydroxyperinaphthenone (Ia). Boekelheide and Larrabee[4] have reported the isolation of a phenolic fraction from the reduction product of perinaphthenone. Also, Koelsch and Anthes[5] have found that the reduction of 9-phenylperinaphthenone (V) led to a phenolic derivative for which they wrote structure VI.





It appears quite likely that 7,9-diketoperinaphthane reacts in the enol form Ia and the absorption of the first molecule of hydrogen occurs by 1,4-addition to afford 1,3-dihydroxyperinaphthene (IV) corresponding to the phenyl analog VI isolated by Koelsch and Anthes. However, in the present instance, the intermediate perinaphthene absorbed a second molecule of hydrogen to afford, as the final product, 1,3-dihydroxyperinaphthane (III).

Similarly, the reduction of 9-methoxyperinaphthenone (VII) in the presence of Raney nickel or copper chromite catalyst afforded a phenolic product, presumably 1-hydroxy-3-methoxyperinaphthane (VIII). Both 1,3-dihydroxyperinaphthane and its monomethyl ether VIII when treated with dimethyl sulfate in aqueous alkali, afforded the identical dimethyl ether derivative, 1,3-dimethoxyperinaphthane (IX).

Experimental[6]

7,9-Diketoperinaphthane (I).—The procedure employed was that of Errera.[7] The compound was obtained as a yellow solid, m.p. 250–254° (unrecrystallized) in 89% yield.

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[1] Beaunit Mills Predoctoral Fellow, 1951–1952. Eastman Kodak Co., Rochester 4, New York.

[2] V. Boekelheide and M. Goldman, This Journal, **76**, 604 (1954).

[3] H. Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, p. 56 ff.

[4] V. Boekelheide and C. E. Larrabee, This Journal, **72**, 1245 (1950).

[5] C. F. Koelsch and J. A. Anthes, *J. Org. Chem.*, **6**, 558 (1941).

[6] Analyses by Miss Claire King.

[7] G. Errera, *Gazz. chim. ital.*, **41I**, 190 (1911).