TABLE II

CONDENSATION OF HYDROXYNAPHTHYL KETONES WITH AROMATIC ALDEHYDES

Ketone	Wt. of Aldehyde,[a] G.	Yield, G. Color React. with Concd. H_2SO_4	M.P., °C.	Formula	Analyses, %
Ia	0.3 (A)	0.9 Orange	268	$C_{31}H_{24}O_4$ VIa	Calcd.: C, 80.9; H, 5.3 Found: C, 80.9; H, 5.4
Ib	0.3 (A)	0.7 Orange	202	$C_{33}H_{28}O_4$ VIb	Calcd.: C, 81.1; H, 5.8 Found: C, 81.0; H, 5.8
Ic	0.3 (A)	0.5 Orange	122	$C_{35}H_{32}O_4$ VIc	Calcd.: C, 81.4; H, 6.2 Found: C, 81.4; H, 6.3
Ia	0.4 (B)	1.2 Deep brown	310	$C_{31}H_{23}NO_6$ VId	Calcd.: C, 73.7; H, 4.6; N, 2.8 Found: C, 74.3; H, 4.7; N, 2.9
Ib	0.4 (C)	0.8 Orange	228	$C_{33}H_{27}ClO_4$ VIe	Calcd.: C, 75.8; H, 5.2; Cl, 6.8 Found: C, 75.7; H, 5.4; Cl, 6.9

[a] A, Benzaldehyde; B, *p*-nitrobenzaldehyde; C, *o*-chlorobenzaldehyde.

Dioxime of IIb crystallizes as yellow crystals from dilute ethyl alcohol, m.p. 235–236°. It is soluble in sodium hydroxide solution, dissolves in concentrated sulfuric acid yielding yellowish green solution and its alcoholic solution gives deep green color with ferric chloride solution.

Anal. Calcd. for $C_{27}H_{26}N_2O_4$: C, 73.3; H, 5.9; N, 6.3. Found: C, 73.4; H, 6.2; N, 6.1.

Acetylation of V. The diacetyl derivative was crystallized from benzene as colorless crystals, m.p. 194°. It gives yellow color with concentrated sulfuric acid.

Anal. Calcd. for $C_{29}H_{24}O_6$: C, 74.3; H, 5.2. Found: C, 74.7; H, 5.4.

Condensation of hydroxynaphthyl ketones with aromatic aldehydes. The ketone (I) (1 g.) and the aromatic aldehyde were dissolved in 30 ml. of glacial acetic acid. The solution was cooled to about 5°, and four drops of concentrated sulfuric acid were added. The solution was kept at about 5° in a tightly stoppered flask for 7 days. The yellow solid that separated was filtered and washed with hot ethyl alcohol and crystallized from benzine (b.p. 100–120°). VId was crystallized from toluene. VIa–VIe are insoluble in aqueous sodium hydroxide solution and give a green color with ferric chloride solution.

DEPARTMENTS OF CHEMISTRY
CAIRO UNIVERSITY AND
A'IN SHAMS UNIVERSITY
CAIRO, EGYPT

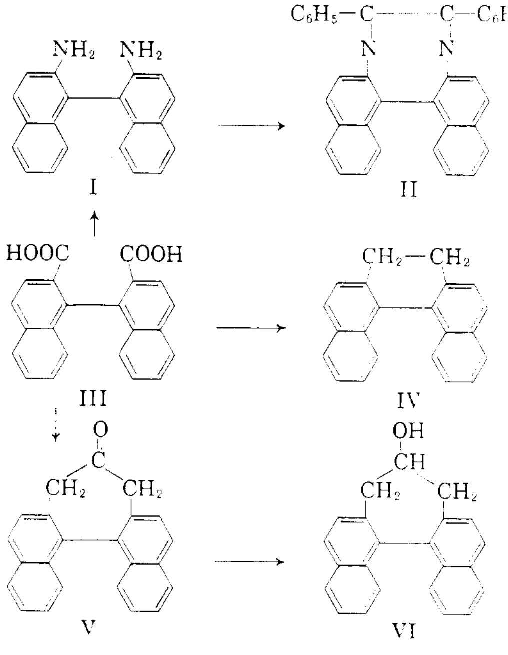
Absolute Configuration of 1,1'-Bi-2-naphthylamine[1]

KURT MISLOW AND PAUL A. GRASEMANN

Received July 7, 1958

According to a recently formulated optical displacement rule,[2] the fact that (+)-1,1'-bi-2-naphthylamine (I) gives the strongly levorotatory bridged derivative[3] II suggests that (+)-I has the (*R*)-configuration.[4] This conclusion is buttressed by the observation[3] that both (+)-I and (+)-(*R*)-6,6'-dimethyl-2,2'-biphenyldiamine[5] change optical sign in acidic solvents. In the present work we have provided sound support for this configurational assignment.

The absolute configuration of 1,1'-binaphthalene-2,2'-dicarboxylic acid (III) has previously been secured by three independent lines of evidence. First, the (*R*)-configuration has been established[2] for (−)-IV, a derivative[6] of (+)-III, on the basis of arguments arising out of the polarizability theory of optical activity. Second, (−)-VI, a derivative of (+)-III, has been assigned[7] the (*R*)-configuration on the basis of the fact that a partial Meerwein-



---

(1) Configurational Studies in the Biphenyl Series. VIII. Part VII: Ref. 8.

(2) D. D. Fitts, M. Siegel, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 480 (1958).

(3) R. Kuhn and P. Goldfinger, *Ann.*, **470**, 183 (1929).

(4) Nomenclature according to R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

(5) F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 476 (1958).

(6) D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1242 (1955).

(7) K. Mislow and F. A. McGinn, *J. Am. Chem. Soc.*, in press.

Ponndorf-Verley reduction of (±)-V with (*S*)-2-octanol affords (−)-VI. Third, the observation[8] that reaction of the phenylglyoxylate of (−)-VI with methylmagnesium iodide yields an excess of the (*R*)-atrolactate of (−)-VI has furnished supporting evidence for the stated configurational assignment. The (*R*)-configuration has thus been firmly established for (+)-III.

A Curtius degradation of (−)-(*S*)-III yielded (−)-I, identified by analysis, melting point, mixture melting point, rotation, and infrared spectrum. It follows that (+)-I has the (*R*)-configuration, in harmony with the earlier, more tentative conclusions.

EXPERIMENTAL

A mixture of 10 g. of 1,1′-binaphthalene-2,2′-dicarboxylic acid[6] [m.p. 138–145° dec., $[\alpha]_D^{29.5}$ −78.3° (*c* 0.83, 0.1*N* NaOH)], 92 ml. of thionyl chloride and 3.6 ml. of anhydrous pyridine was refluxed for 45 min. and the resulting orange solution was evaporated to dryness. The residue was taken up in carbon tetrachloride (100 ml.), the solution was filtered, and the filtrate was evaporated to yield 9.1 g. (82%) of the yellow, crystalline acid chloride, m.p. 173–177°. A solution of 8.05 g. of sodium azide in 20 ml. of water was added dropwise to a swirled solution of 8.05 g. of the acid chloride in 80 ml. of acetone; a precipitate formed on contact. The mixture was cooled in an ice bath and 120 ml. of water was added. The initially formed yellowish brown oil solidified on standing at ice bath temperature to yield a beige solid which was collected by centrifugation, washed with water, and dissolved in 120 ml. of benzene. The benzene solution was dried with calcium sulfate. A vigorous evolution of gas was produced when the solution was heated at 60–70°. After the reaction had subsided, the solution was heated under reflux for 1 hr., 50 ml. of 50% aqueous potassium hydroxide was introduced, and refluxing was continued for 1.5 hr. The benzene layer was separated, *ca.* 200 ml. of 6*N* hydrochloric acid was added, and mixture was heated on the steam bath for 15 min. The acid layer was separated, filtered from some gray insoluble material (m.p. >360°), and neutralized with sodium hydroxide. The precipitated amine was washed with water until the washings were neutral to give, after drying, 3.3 g. (40%) of product, m.p. 237–238°. Two recrystallizations from ethanol-benzene yielded a light beige solid, m.p. 242–243.5°, $[\alpha]_D^{30}$ −152.2° (*c* 1.78, benzene).

Anal.[9] Calcd. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.34; H, 5.58; N, 9.81.

A mixture of the product and of authentic[10] (−)-I [m.p. 245°, $[\alpha]_D^{20}$ −156° (*c* 1.0, benzene); lit.[3] m.p. 243°, $[\alpha]_D^{19}$ 183.8° (benzene)] melted at 242–244°; a mixture of the product and of authentic[10] (+)-I [m.p. 244.5–247°, $[\alpha]_D^{20}$ +154° (*c* 0.64, benzene)] had m.p. 195–205°. The infrared spectra (KBr pellet) of the product and of authentic (−)-I were identical.

WM. H. NICHOLS CHEMICAL LABORATORY
NEW YORK UNIVERSITY
NEW YORK 53, N. Y.

---

[8] K. Mislow, V. Prelog, and H. Scherrer. *Helv. Chim. Acta*, **41**, 1410 (1958).

[9] Microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[10] We thank Dr. J. H. Rassweiler for providing us with a sample of that substance.

Oxidation of Organic Sulfides with Dimethyl Sulfoxide

SCOTT SEARLES, JR., AND HUGH R. HAYS

Received July 9, 1958

In the attempted synthesis of a series of dialkyl and cyclic sulfoxides the usual methods of oxidation of the corresponding sulfides were sometimes found unsatisfactory. One of the difficulties is the relative ease of further oxidation of sulfoxide to sulfone. For example, we were unable to obtain di-*t*-butyl sulfoxide by oxidation of di-*t*-butyl sulfide with hydrogen peroxide, nitric acid, or dinitrogen tetroxide, although it was possible to obtain the corresponding sulfone with hydrogen peroxide.

In the hope of finding a mild enough oxidizing agent we attempted the following oxygen exchange reaction, using dimethyl sulfoxide as an oxygen donor:

$$R_2S + Me_2SO \longrightarrow R_2SO + Me_2S$$

It has been known for some time that sulfoxides may serve as oxidizing agents for several inorganic reagents.[1] Also, Kornblum and collaborators in a recent communication reported the successful oxidation of several phenacyl halides with dimethyl sulfoxide.[2] In the present work, we attempted the dimethyl sulfoxide oxidation of several higher molecular weight sulfides.

Dimethyl sulfoxide was found to oxidize *n*-propyl, *n*-butyl, and tetramethylene sulfides to the corresponding sulfoxides in yields of 59, 55, and 58%, respectively. The conditions employed involved heating the sulfide with a 50% molar excess of dimethyl sulfoxide at 160–175° for several hours. Dimethyl sulfide was removed by distillation, as formed.

The structures of the products were shown by identity of melting points and/or boiling points and the infrared spectra with those of authentic samples. It was of interest that the sulfoxides were isolated in high purity by simple distillation, as shown by their melting points and infrared spectra. There was no evidence of any sulfone formation. Unfortunately, several similar sulfides did not react appreciably with dimethyl sulfoxide under these conditions, and attempts to catalyze the reactions with acid were unsuccessful.

EXPERIMENTAL

General procedure. A mixture of 0.1 mole of dialkyl sulfide and 0.15 mole of dimethyl sulfoxide[3] was heated at 160–

---

[1] R. Connor, in H. Gilman's, *Organic Chemistry*, John Wiley & Sons, New York, N. Y., 1943, Vol. I, p. 872.

[2] N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).

[3] We are indebted to the Stepan Chemical Co. for a generous gift of dimethyl sulfoxide.