and distilled into two portions, (I) b. p. 156–161, n^{20}D 1.4247–1.4320; (II) b. p. 162–165, n^{20}D 1.4325–1.4380.

Refractionation of the lower boiling fractions (I) through Column A gave material boiling at 152–162°, n^{20}D 1.4297–1.4336. Ozonolysis of this material gave formaldehyde, trimethylacetaldehyde and pinacolone, identified as their 2,4-dinitrophenylhydrazones.[12] Hydrogenation of these lower boiling fractions gave material boiling mainly at 165°, n^{20}D 1.4216.

Refractionation of the higher boiling portion (II) through Column B gave material of b. p. 162–166°, n^{20}D 1.4314–1.4396. This when hydrogenated gave material boiling mainly at 171°, n^{20}D 1.4278–90, having a mol. wt. of 166 (dodecane = 168) and which was insoluble in cold concd. sulfuric acid.

Physical Properties.—The constants determined for the hydrocarbons are given the accompanying table. The boiling points were measured in a Cottrell-type apparatus using a thermometer with 0.2° divisions checked against a Bureau of Standards calibrated Anschutz thermometer. Refractive indices were read on a Valentine No. 454 refractometer. Densities were measured in pycnometers; and viscosities, with the Ostwald-type viscometer recommended by Cannon and Fenske[13] for use with non-viscous liquids.

The physical properties were determined by N. C. Cook and Andrew Carson; some of the hydrogenations were performed by R. E. Meyer and N. C. Cook.

Summary

Four highly branched hydrocarbons, 2,2,4-trimethylheptane, 2,2,4-trimethyloctane, 2,2,4,6-tetramethylheptane, and 2,2,4,5,5-pentamethylhexane have been synthesized and a number of their physical properties determined.

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[12] Identification by H. H. Johnson, Ph.D. Thesis, Penn State, 1940.

[13] Cannon and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 299 (1938).

STATE COLLEGE, PA. RECEIVED OCTOBER 22, 1948

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

Substituted 1,10-Phenanthrolines. II. Di- and Tri-methyl Phenanthrolines Related to 5-Methyl-1,10-phenanthroline[1]

BY FRANCIS H. CASE

Continuing the work described in the first article of this series[2] with the object of preparing a series of substituted phenanthrolines which in the form of their ferrous complexes would be suitable for use as oxidation–reduction indicators, all possible di- and tri-methyl-1,10-phenanthrolines were synthesized in which one methyl group is in the 5- or 6- position and each of the others in a different ring, but none adjacent to nitrogen. The quinolines and phenanthrolines described here were synthesized from a substituted aniline or aminoquinoline by a Skraup reaction using arsenic acid as oxidizing agent and either glycerol, α-methylacrolein diacetate (2-methyl-2-propene-1,1-diol diacetate) or methyl vinyl ketone as the second component. In the case of 3,5-dimethyl-8-nitroquinoline this method proved much more satisfactory than that previously described,[3] while with 4,5-dimethyl-8-nitroquinoline no improvement in yield was noted.

Under these conditions 3,5-dimethyl-1,10-phenanthroline (III) was obtained from 6-methyl-8-aminoquinoline[4] (II) and α-methylacrolein diacetate.

The action of α-methylacrolein diacetate and 3-nitro-4-aminotoluene (I) yielded, in a two-step reaction, 3,6-dimethyl-8-aminoquinoline (IV) which with glycerol was converted to 3,6-dimethyl-1,10-phenanthroline (V).

I, with methyl vinyl ketone under Skraup conditions yielded in a two-step reaction 4,6-dimethyl-8-aminoquinoline (VI) from which the following compounds were made: 3,5,7-trimethyl-1,10-phenanthroline (VII) (with α-methylacrolein diacetate); 4,6-dimethyl-1,10-phenanthroline (VIII) (with glycerol); 4,5,7-trimethyl-1,10-phenanthroline (IX) (with methyl vinyl ketone). From 3,5-dimethyl-8-aminoquinoline (XI) and α-methylacrolein diacetate, 3,5,8-trimethyl-1,10-phenanthroline (XII) was obtained. This also resulted in very small yield if 3,6-dimethyl-8-aminoquinoline (IV) were used as the base. From 4,5-dimethyl-8-aminoquinoline (XIII) and glycerol, 4,5-dimethyl-1,10-phenanthroline (XIV) resulted, while if α-methylacrolein diacetate were used as the second component, 3,6,7-trimethyl-1,10-phenanthroline (XV) was formed.

It should be noted that in the synthesis of each substituted phenanthroline two possible methods were available. For example, 4,5-dimethyl-1,10-phenanthroline might theoretically be prepared by the action of 4,5-dimethyl-8-aminoquinoline with glycerol or of 6-methyl-8-aminoquinoline with methyl vinyl ketone. Both methods were tried, but in the latter case, no yield was obtained. The choice of methods was conditioned by the availability of the starting aminoquinoline as well as by the fact that the yield is highest when glycerol is used as the second component, less with α-methylacrolein diacetate and least with methyl vinyl ketone. When both possible methods were attempted this fact is indicated by a footnote in Table I.

All the phenanthrolines described in this paper give a positive ferroin reaction.

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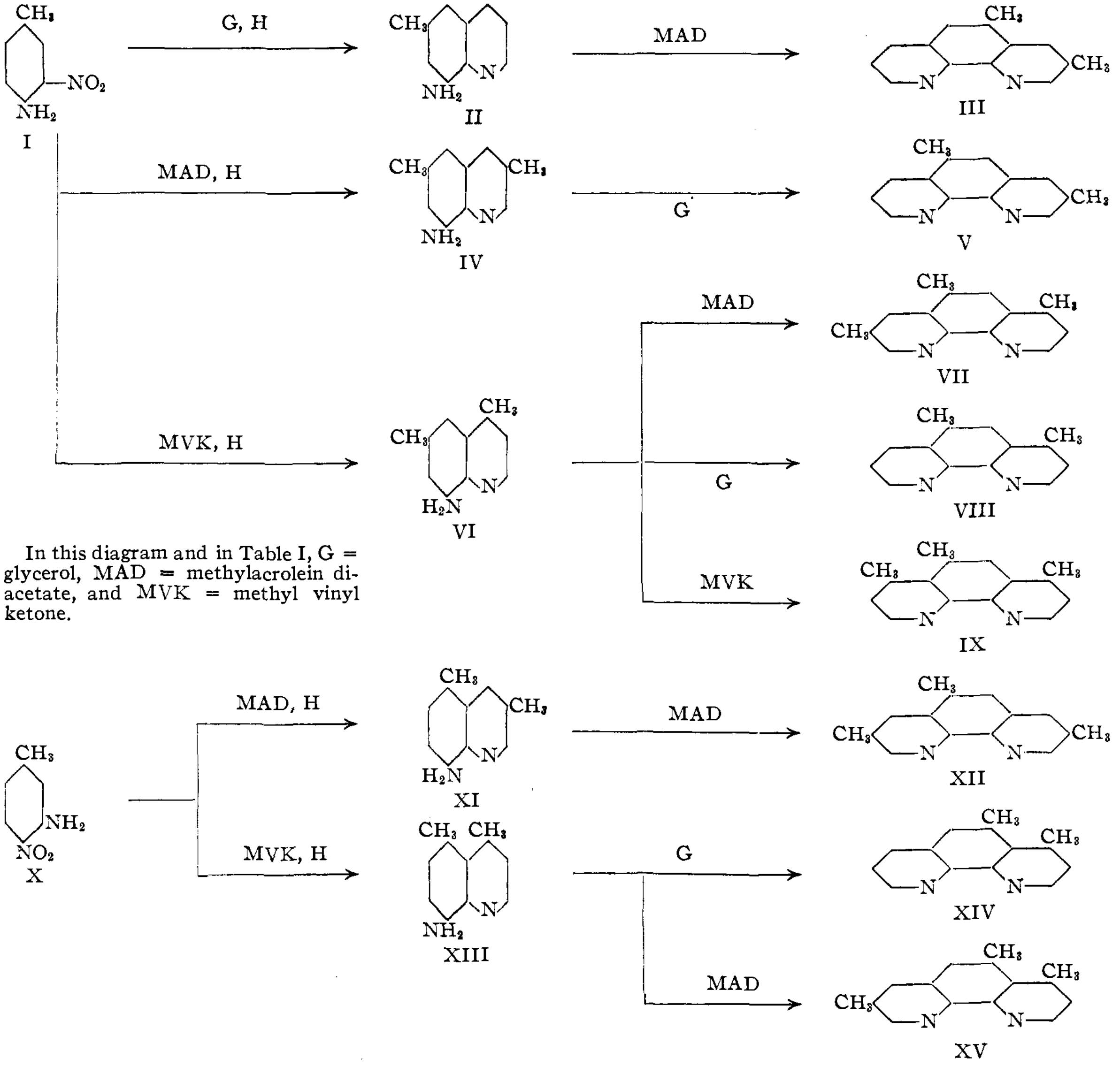
[1] This work was supported by a Grant from the Committee on Research and Publications of Temple University.

[2] Case, THIS JOURNAL, **70**, 3994 (1948).

[3] Manske, *Can. J. Res.*, **20B**, 133 (1942).

[4] Baldwin, *J. Chem. Soc.*, 2959 (1929).



In this diagram and in Table I, G = glycerol, MAD = methylacrolein diacetate, and MVK = methyl vinyl ketone.

Experimental

Methyl Vinyl Ketone.—The cooled azeotrope obtained from du Pont containing 15% water, was shaken with anhydrous potassium carbonate, dried over calcium chloride and distilled *in vacuo*. The resulting liquid nearly all boiled at 34–40° (150 mm.).

4,6-Dimethyl-8-nitroquinoline.—A mixture of 25.3 g. of 2-nitro-4-methylaniline, 36 ml. of concentrated sulfuric acid, 12 ml. of water and 25.0 g. of arsenic oxide was warmed to 100°. Methyl vinyl ketone (17 g.) was then added at such a rate that the temperature did not exceed 140°. The mixture was maintained at this temperature for two hours with stirring, then poured on ice, and made alkaline with sodium hydroxide. The resulting precipitate was removed by filtration, dried, and extracted with hot benzene. Removal of the benzene and crystallization from the same solvent yielded 12 g. of pure product, m.p. 147–148°; yield, 35.6%.

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98. Found: C, 65.24; H, 4.76.

4,6-Dimethyl-8-aminoquinoline.—This compound was obtained by reduction of the nitro compound (67 g.) with 229 g. of $SnCl_2 \cdot 2H_2O$ in 1200 ml. of boiling ethanol; yield, 51 g., b.p. 195–205° (9 mm.). The pure substance, on crystallization from petroleum ether, melts at 85–86°.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02. Found: C, 77.18; H, 6.99.

3,6-Dimethyl-8-nitroquinoline.—The preparation of this compound was identical with that of 4,6-dimethyl-8-nitroquinoline, the same amounts of materials being used except that 50 g. of α-methylacrolein diacetate was substituted for methyl vinyl ketone. The yield of product, melting at 163–164° after crystallization from benzene was 11.5 g. or 34.2%.

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98. Found: C, 65.75; H, 4.97.

3,6-Dimethyl-8-aminoquinoline.—Reduction of 57 g. of the corresponding nitro compound by 193 g. of $SnCl_2 \cdot 2H_2O$ in 1100 ml. of boiling ethanol yielded 32 g. of 3,6-dimethyl-8-aminoquinoline, b.p. 202–220° (5 mm.). The pure product melts at 107–108° after crystallization from benzene-petroleum ether.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02. Found: C, 76.95; H, 7.47.

TABLE I

1,10-Phenanthroline	1st component, quinoline	2nd component	M. p., °C.	Yield, %	Analyses,[d] % Calcd. C	H	Found C	H
3,5-Dimethyl	6-Methyl-8-amino-	MAD	169–170	4.2	80.74	5.81	80.90	5.44
4,5-Dimethyl[a,c]	4,5-Dimethyl-8-amino-	G	151–152	24.0	80.74	5.81	80.42	5.73
3,6-Dimethyl[b,c]	3,6-Dimethyl-8-amino-	G	117–118	2.6	80.74	5.81	80.49	5.93
4,6-Dimethyl	4,6-Dimethyl-8-amino-	G	161–162	11.4	80.74	5.81	80.67	5.73
3,5,7-Trimethyl	4,6-Dimethyl-8-amino-	MAD	201–202	14.5	81.05	6.35	81.21	6.10
3,5,8-Trimethyl[c]	3,5-Dimethyl-8-amino-	MAD	185–186	8.7	81.05	6.35	80.78	6.12
3,6,7-Trimethyl[a,c]	4,5-Dimethyl-8-amino-	MAD	177–178	2.1	81.05	6.35	81.07	6.24
4,5,7-Trimethyl	4,6-Dimethyl-8-amino-	MVK	184–185	1.3	81.05	6.35	80.84	6.37

[a] These samples are hygroscopic. [b] Crystallized from benzene–petroleum ether. [c] Alternate method tried, but yield of phenanthroline negligible. [d] Analyses were done by the Clark Microanalytical Laboratory, Urbana, Illinois.

3,5-Dimethyl-8-nitroquinoline.[3]—The preparation of this compound was similar to that of 3,6-dimethyl-8-nitroquinoline except that 2-nitro-5-methylaniline was used as the first component; yield, 9.5 g. or 28.0%, m.p. 189–190° (from 25.5 g. of 2-nitro-5-methylaniline).

4,5-Dimethyl-8-nitroquinoline.[3]—This compound was prepared exactly as in the case of 4,6-dimethyl-8-nitroquinoline except that 2-nitro-5-methylaniline was used as the first component; yield, 3 g. or 8.9%, m.p. 139–140° (from 25.3 g. of 2-nitro-5-methylaniline).

General Procedure for the Synthesis of Di- and Trimethyl-1,10-Phenanthrolines.—A mixture of one molar proportion of the appropriate methyl- or dimethyl-8-aminoquinoline, 0.65 mole of arsenic oxide, 4 moles of sulfuric acid in 96.8% solution and a volume of water equal to one third of the volume of sulfuric acid used was heated to 100° and treated with glycerol (3.6 moles), α-methylacrolein diacetate (1.8 moles), or methyl vinyl ketone (1.8 moles) at such a rate that the temperature did not exceed 140°. It was then heated with stirring for two more hours at this temperature. The mixture was then poured into water, made alkaline, and the tarry precipitate removed by filtration. The filtrate was extracted three times with hot benzene, which was then used to extract the phenanthroline from the solid material. After removal of the benzene the phenanthroline was crystallized from benzene. The results are shown in Table I.

Summary

The following phenanthrolines have been synthesized: 3,5-, 4,5-, 3,6-, 4,6-dimethyl- and 3,5,7-, 3,5,8-, 3,6,7- and 4,5,7-trimethyl-1,10-phenanthrolines.

3,6- and 4,6-dimethyl-8-nitroquinolines and the corresponding amino derivatives have been prepared.

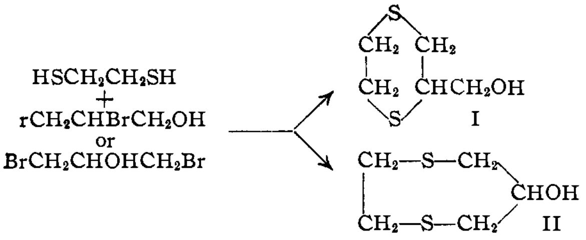
RECEIVED AUGUST 17, 1948

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

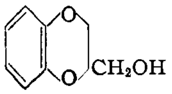
Formation of a Seven-membered Cyclic Disulfide from 1,2-Dibromohydrin and a 1,2-Dithiol

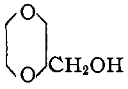
BY REYNOLD C. FUSON AND A. JOHN SPEZIALE[1]

In connection with other studies, an attempt was made to prepare 2-hydroxymethyl-1,4-dithiane (I) and 6-hydroxy-1,4-dithiacycloheptane (II) by condensing ethanedithiol with 2,3-dibromo-1-propanol and 1,3-dibromo-2-propanol, respectively. It was found that the two reactions yielded the same product—the carbinol with the seven-membered ring (II).



It had been observed that, in the preparation of acyclic diethers from 1,2- or 1,3-dihalohydrins or from epihalohydrins, the 1,3-diethers are produced in preference to the 1,2-diethers.[2] In the formation of cyclic ethers, however, it was to be expected that a six-membered ring would be produced to the exclusion of a seven-membered ring as observed in the synthesis of 2-hydroxymethyl-1,4-benzodioxane (III) from pyrocatechol and the dihalohydrins,[3] and of 2-hydroxymethyl-1,4-dioxane (IV) from ethylene glycol and epichlorohy-


III


IV

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[1] American Chemical Society Predoctoral Fellow, 1946–1947; present address: Monsanto Chemical Company, St. Louis, Mo.

(2) (a) Gilchrist and Purvis, *J. Chem. Soc.*, **127**, 2735 (1925); (b) Zunino, *Atti. accad. Lincei*, **6**, 348 (1897); *J. Chem. Soc.*, **76**, 410 (1899); (c) Rossing, *Ber.*, **19**, 63 (1886); (d) Lindemann, *ibid.*, **24**, 2145 (1891); (e) Fairbourne, *J. Chem. Soc.*, 1151 (1929); (f) Fairbourne, Gibson and Stephens, *ibid.*, 1965 (1932); (g) Fairbourne, Gibson and Stephens, *ibid.*, 445 (1931); (h) Boyd, *ibid.*, **79**, 1221 (1901); (i) Boyd and Marle, *ibid.*, **93**, 838 (1908); (j) Delaby and Dubois, *Bull. soc. chim.*, **47**, 565 (1930).

(3) (a) Moureu, *Ann. chim. phys.*, **18**, 76 (1899); (b) Fourneau, *J. pharm. chim.*, **1**, 55 (1910); (c) French Patent 770,485, September 14, 1934; (d) U. S. Patent 2,366,661, January 2, 1945.