present interest was the mechanism of the specific ethanol–butadiene process as operated.

TABLE IX

NON-OPERATIVE FEEDS

1,4-Dioxane
Ethanol-1,4-dioxane
Butadiene monoxide
Tetrahydrofuran
Thiophene
Ethanol–thiophene
Dioxolane
2-Methyl-1,3-dioxolane
Ethanol-2-methyl-1,3-dioxolane
Ethanol–glyoxal hydrate
Ethanol–ethyl vinyl ether
Pyrrole
1,2-Butanediol
Ethanol–water–pyrrole
Ethylene–ethyl vinyl ether
Ethylene–acetal
Ethanol–water–diethyl ether
Ethanol–water–ethyl acetate
Ethanol–water–ethylene
Acetaldehyde
Acetaldehyde–water–diethyl ether
Cyclohexanol–acetaldehyde
Cyclohexene
Cyclohexene–acetaldehyde
Ethyltetralin–acetaldehyde
Ethyltetralin–ethylene oxide
2,3-Butanediol (*levo* and *meso* with and without ethanol)

Acknowledgment.—Thanks are expressed to J. Cohen and B. J. Steenbergen for assistance in the experimental work; to G. C. Akerlof, J. R. Bowman and P. H. Emmett for valuable comments; and to L. H. Cretcher and E. R. Weidlein for friendly encouragement.

Summary

1. The rate controlling process in the second step of the ethanol–butadiene process at atmospheric pressure is a second order condensation of acetaldehyde to crotonaldehyde, whereas at pressures of 4–30 atmospheres the rate of consumption of acetaldehyde is of first order.

2. The final reaction which produces butadiene is the deoxygenation of crotonaldehyde by ethanol.

3. A mixture of crotyl alcohol with a minor amount of crotonaldehyde is ideal for the production of butadiene under the conditions of the ethanol–butadiene process (60 mole % yield per pass).

4. Feed mixtures capable of producing acetaldehyde (or crotonaldehyde) *in situ* produce butadiene when processed over Ta_2O_5–SiO_2 catalyst.

5. The primary function of the silica component of the commercial catalyst is to catalyze the condensation of acetaldehyde, whereas the function of the tantala promoter is to catalyze the deoxygenation of crotonaldehyde by ethanol.

6. Numerous mechanisms proposed by various investigators were demonstrated to be inoperative under the conditions of the second step of the American ethanol–butadiene process.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

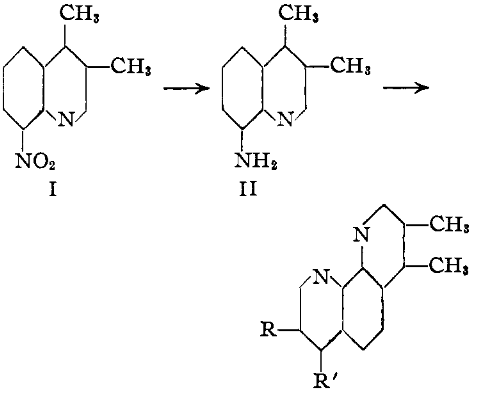
Substituted 1,10-Phenanthrolines. III.[1,2] Polymethyl Phenanthrolines Related to 3,4-Dimethyl-1,10-phenanthroline

BY FRANCIS H. CASE

The use of 1-hydroxy-2-methyl-3-butanone, $CH_3COCH(CH_3)CH_2OH$, as a reactant in the Skraup synthesis has been limited[3,4] to the synthesis of 3,4-dimethylquinoline. In this Laboratory a series of polymethyl-1,10-phenanthrolines has been prepared by the use of the above keto alcohol with the object of furnishing derivatives which in the form of their ferrous complexes would be likely to have a low oxidation potential.

The action of *o*-nitroaniline and 1-hydroxy-2-methyl-3-butanone under Skraup conditions yielded 3,4-dimethyl-8-nitroquinoline I (see diagram). The corresponding aminoquinoline II under Skraup conditions yielded 3,4-dimethyl-1,10-phenanthroline III (with glycerol); 3,4,7,8-tetramethyl-1,10-phenanthroline IV (with 1-hydroxy-2-methyl-3-butanone); 3,4,8-trimethyl-1,10-phenanthroline V (with methylacrolein diacetate (2-methyl-2-propene-1,1-diol diacetate); and 3,4,7-trimethyl-1,10-phenanthroline VI (with methyl vinyl ketone).

The action of 2-nitro-4-methylaniline and 1-hydroxy-2-methyl-3-butanone yielded 3,4,6-trimethyl-8-nitroquinoline VII. The corresponding amine VIII yielded on reaction with glycerol, 3,4,6-trimethyl-1,10-phenanthroline IX; with methylacrolein diacetate, 3,4,6,8-tetramethyl-1,10-phenanthroline X; and with methyl vinyl



II + G → III R and R′ = H
II + MB → IV R and R′ = CH_3
II + MAD → V R = CH_3, R′ = H
II + MVK → VI R = H, R′ = CH_3

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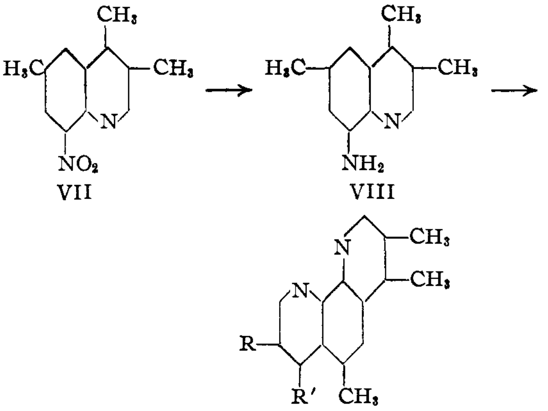
[1] For other papers in this series see Case, THIS JOURNAL, **70**, 3994 (1948), and **71**, 821 (1949).

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

[3] Prill and Walter, United States Patent, 1,806,563 (1931).

[4] Manske, Marion and Leger, *Can. J. Res.*, **20B**, 133 (1942).



VII VIII

VIII + G ⟶ IX R and R' = H
VIII + MAD ⟶ X R = CH_3, R' = H
VIII + MVK ⟶ XI R = H, R' = CH_3

In this diagram, G = glycerol, MAD = methylacrolein diacetate, MVK = methyl vinyl ketone, and MB = 1-hydroxy-2-methyl-3-butanone.

ketone, 3,4,6,7-tetramethyl-1,10-phenanthroline XI.

Attempts to bring about Skraup reactions between 1-hydroxy-2-methyl-3-butanone and the following were unsuccessful: 2-nitro-5-methylaniline, 2-nitro-4,5-dimethylaniline, and 3,4,6-trimethyl-8-aminoquinoline.

All the phenanthrolines described give a positive ferroin reaction.

Experimental

3,4-Dimethyl-8-nitroquinoline.—A mixture of 35 g. of *o*-nitroaniline, 37 g. of arsenic oxide, 54 ml. of concentrated sulfuric acid, and 9 ml. of water was warmed to 100°. 1-Hydroxy-2-methyl-3-butanone[5] (39 g.) was then added at such a rate that the temperature did not exceed 140°. Heating was continued, with stirring, at this temperature for two more hours. The reaction mixture was then poured into ice water 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 product melting at 149-150°. The pure product melts at 152-155° after repeated crystallization.

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98. Found: C, 65.32; H, 5.00.

3,4-Dimethyl-8-aminoquinoline.—This was prepared by the reduction of the nitro derivative (52 g.) by 178 g. of $SnCl_2{\cdot}2H_2O$ in 900 ml. of boiling ethanol; yield, 36.5 g. of product, b. p. 190-195 (7 mm). This substance, which solidifies on standing, was crystallized from petroleum ether. It melts at 98-99°.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02. Found: C, 76.53; H, 7.06.

3,4,6-Trimethyl-8-nitroquinoline.—This was prepared from 4-methyl-2-nitroaniline, using the same molar proportions and procedure as for 3,4-dimethyl-8-nitroquinoline; m. p. 193-195°, yield, 17%. The pure product, after recrystallization from benzene, melts at 198-199°.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59. Found: C, 66.81; H, 5.88.

3,4,6-Trimethyl-8-aminoquinoline.—From 50.5 g. of 3,4,6-trimethyl-8-nitroquinoline and 160 g. of $SnCl_2{\cdot}2H_2O$ in 1 liter of alcohol was obtained 30.5 g. of base melting at 126-127° after crystallization from alcohol.

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.70; H, 7.32.

General Procedure for the Synthesis of Polymethyl-1,10-phenanthrolines.—A mixture of one molar proportion of the appropriate dimethyl- or trimethyl-8-aminoquinoline, 0.7 mole of arsenic oxide, 4 moles of sulfuric acid in 97% solution, and a volume of water equal to one-third (with 1-hydroxy-2-methyl-3-butanone, one-fourth) of the volume of sulfuric acid used was heated to 100° and treated with glycerol (4 moles), methylacrolein diacetate, methyl vinyl ketone, or 1-hydroxy-2-methyl-3-butanone (1.8 moles each) at such a rate that the temperature did not exceed 140°. It was kept at this temperature, with stirring, for two more hours. The mixture was then poured into water, made alkaline, and the precipitate removed by filtration. The filtrate was extracted three times with hot benzene, which was then used to extract the phenanthroline from the precipitate. After removal of the benzene, the phenanthroline was crystallized from benzene. The results are shown in Table I.

TABLE I[a]

1,10-Phenanthroline[b]	M. p., °C.	Yield, %	Composition, % C Calcd.	C Found	H Calcd.	H Found
3,4-Dimethyl	234-235	22.3	80.74	80.75	5.81	6.04
3,4,8-Trimethyl	211-212	9.1	81.05	81.01	6.35	6.40
3,4,7-Trimethyl	221-222	30.9	[c]	...	..	..
3,4,6-Trimethyl	217-218	18.6	81.05	80.76	6.35	6.39
3,4,6,8-Tetramethyl	189-190	8.8	81.32	81.15	6.83	6.97
3,4,6,7-Tetramethyl	229-230	4.9	81.32	81.26	6.83	6.59
3,4,7,8-Tetramethyl	275-276	20.2	81.32	81.08	6.83	6.47

[a] The analyses were done by the Clark Microanalytical Laboratory, Urbana, Illinois. [b] These phenanthrolines are being tested as to stability and oxidation potential of their ferrous complexes by Dr. G. Frederick Smith. [c] *Anal.* Calcd. for $C_{16}N_2H_{14}$: N, 12.61; Found: N, 12.55.

Summary

The following substituted 1,10-phenanthrolines have been prepared: 3,4-dimethyl; 3,4,6-, 3,4,7-, 3,4,8-trimethyl; 3,4,6,7-, 3,4,6,8-, 3,4,7,8-tetramethyl. All give the ferroin test.

3,4-Dimethyl- and 3,4,6-trimethyl-8-nitroquinoline and their corresponding amino compounds have been synthesized.

RECEIVED NOVEMBER 12, 1948

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[5] Morgan, *Chemistry and Industry*, **57**, 885 (1938).