and on simplifying $= x/tb(b - x)$. This, of course, when $b = a$, becomes $x/ta(a - x)$, which is expression (1).

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THE SKRAUP REACTION WITH CERTAIN AZO COMPOUNDS

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In the course of an investigation of the possible explanation of the reaction mechanism of the formation of *p*-phenanthroline in the Skraup reaction with *p*-aminoresorcin dimethyl ether, *p*-benzene-azo-resorcin dimethyl ether was subjected to the Skraup reaction and the product was found unexpectedly to be also *p*-phenanthroline; the yield in this case was three times as good as in the same reaction with *p*-aminoresorcin dimethyl ether. The formation of *p*-phenanthroline was also established, in the same way, from *p*-benzene-azo-resorcin, whereas from *p*-aminoresorcin, no crystalline matter could be isolated, on working under the same conditions.

From these facts it seemed that in case of the Skraup reaction with rather unstable amines, better results might follow if the corresponding azo compounds were used as reactants, and here I have extended this study to several azo compounds.

Concerning the study of the Skraup reaction with azo compounds, work has been reported by Claus and Stegelitz[1] and later by Lellmann and Lippert.[2] They established the formation of the corresponding ring compounds in this reaction, but the yield in each case was reported to be very poor. In the present investigation the reactions were carried out with the addition of arsenic acid, this being the only difference from the methods of previous investigations.

TABLE I

EFFECT OF ARSENIC ACID IN THE SKRAUP REACTION WITH AZO COMPOUNDS

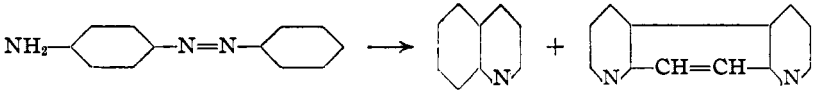
Reactants	Products	Yield, g. Presence of H_3AsO_4	Yield, g. Absence of H_3AsO_4
Azobenzene, 10 g.	Quinoline picrate	0.5	0.55
	6,6'-Diquinolyl	5.7	1.2
p-Benzene-azo-resorcin dimethyl ether	Quinoline	2.0–2.5	1.4
	p-Phenanthroline	1.35–1.5	0.3

[1] Claus and Stegelitz, *Ber.*, 17, 2380 (1884).

[2] Lellmann and Lippert, *ibid.*, 24, 2623 (1891).

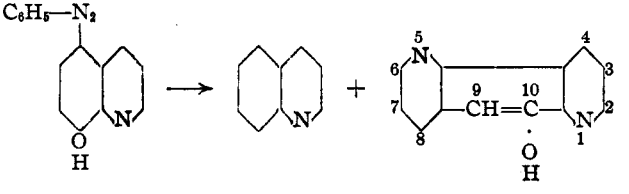
First of all, in order to find the influence of the presence of arsenic acid in the reaction, the following two pairs of experiments were performed for the sake of comparison, with the result that, in the Skraup reaction with azo compounds, the presence of arsenic acid gave far better yields (Table I).

In view of this fact, it seems that the action of arsenic acid in the Skraup reaction may be other than it has previously been thought to be. In the Skraup reaction with *p*-amino-azobenzene, *p*-phenanthroline could be isolated in a satisfactory yield in accordance with the scheme



The preparation of *p*-phenanthroline was reported by Kaufmann and Radošević[3] by the Skraup reaction with 6-aminoquinoline and recently by Smith by the same reaction with *p*-phenylenediamine.[4] The Skraup reaction with *p*-amino-azobenzene, however, appears to be the most suitable for preparing it in quantity, because *p*-amino-azobenzene is more easily accessible than 6-amonoquinoline or *p*-phenylenediamine.

In the Skraup reaction with benzene-azo-5-hydroxy-8-quinoline, the yield of 10-hydroxy-*m*-phenanthroline was very poor on working up under a variety of conditions.

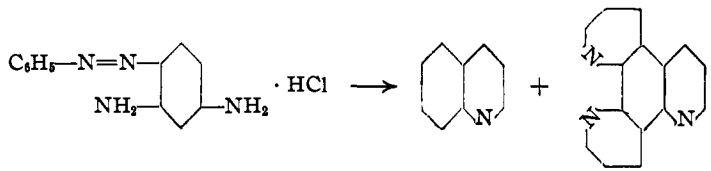


La Coste,[5] in the Skraup reaction with *m*-nitraniline, could isolate an hydroxy-*m*-phenanthroline (m. p. 159–60°) as a by-product and, as to the position of the hydroxyl group, he concluded, under his reasonable interpretation, that the substance might be 2-hydroxy-*m*-phenanthroline.

The hydroxy-*m*-phenanthroline he had obtained appears to be very near in its properties to 10-hydroxy-*m*-phenanthroline (m. p. 157–158°), which I have now obtained.

Pictet and his co-worker[6] obtained phenotripyridine in good yields in the Skraup reaction with 1,3,5-triaminobenzene. Chrysoidin was now submitted to the Skraup reaction, with the expectation of obtaining one of its structural isomers in accordance with the equation

[3] Kaufmann and Radošević, *Ber.*, **42**, 2612 (1909).
[4] Smith, THIS JOURNAL, **52**, 397 (1930).
[5] La Coste, *Ber.*, **16**, 674 (1883).
[6] Pictet and Barbier, *Bull. soc. chim.*, [3] **13**, 28 (1895).



After a tedious process of separation, a minute amount of colorless needles (m. p. 155–156°) could be isolated by means of petroleum ether but the scarcity of the material has rendered its further characterization impossible.

Experimental

General Procedure for the Skraup Reaction with Azo Compounds.—A mixture of monoazo compound ($^1/_{20}$ mole), glycerin (18 g.), concd. sulfuric acid (18 g.) and arsenic acid (9 g.) was gently refluxed in an oil-bath (bath temperature 160–195°) for two to thirty hours. The flask contents, which consisted of a hard black lump on cooling, was digested with hot water and the filtered liquid, after being made alkaline, was distilled with steam. The distillate was shaken with ether. On evaporating the solvent, after thorough drying with sodium sulfate, quinoline could be isolated. It was identified by converting it into its picrate.

From the residue of the steam distillation, by means of benzene, another component of the products could be isolated. Further purification was effected by recrystallization of its sulfate from hot alcohol.

In the case of 10-hydroxy-*m*-phenanthroline, instead of benzene extraction, the material was extracted first with cold alcohol, then with benzene, ether and petroleum ether successively.

Table II

Skraup Reactions

	Reactant	G.	Reaction time, hrs.	Products	Yield, g.
1	*p*-Benzene-azoresorcin dimethyl ether	10	21	Quinoline	2.5
				p-Phenanthroline	1.5
2	*p*-Benzene-azoresorcin	8.85	15	Quinoline	2.3
				p-Phenanthroline	0.07
3	Azobenzene	10	15	Quinoline picrate	0.5
				6,6'-Diquinolyl	5.7
4	*p*-Amino-azobenzene	10	30	Quinoline	2.5
				p-Phenanthroline	7.7
5	*p*-Nitrobenzene-azo-4-naphthol-1	15	21	*p*-Phenanthroline	3.2
6	*p*-Chlorobenzene-azo-phenol	10	21	6-Chloroquinoline	5.2
7	Benzene-azo-5-hydroxy-8-quinoline	15	2	Quinoline	2.6
				10-Hydroxy-*m*-phenanthroline	0.25
8	Chrysoidine	20	3	Quinoline	2.5
				Minute amount of crystals	..

TABLE II (*Concluded*)

Compound	Properties	M. p., °C.
1 Quinoline picrate	Citron yellow needles from benzene	203
1 *p*-Phenanthroline	Colorless needles from benzene	173
2 Quinoline picrate	.....	203
2 *p*-Phenanthroline	.....	173
3 Quinoline picrate	.....	203
3 6,6′-Diquinolyl	Colorless plates of silky luster from dilute alcohol	179–180
4 Quinoline picrate	.....	203
4 *p*-Phenanthroline	.....	173
5 *p*-Phenanthroline	.....	171–172
6 6-Chloroquinoline picrate	Colorless prisms from benzene	41–42
	Yellow hair-like needles from acetone	217
7 Quinoline picrate	.....	203
7 10-Hydroxy-*m*-phenanthroline	Colorless needles from benzene. Soluble in dil. HCl and NaOH. Ferric chloride reaction is dark violet	157–158
8 Quinoline picrate	.....	203
8 Minute amt. crystals	Colorless needles from petroleum ether. Soluble in dil. HCl	155–156

Compound	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
1 Quinoline picrate	50.28	50.35	2.79	2.85	15.64	15.75
1 *p*-Phenanthroline	80.00	80.19	4.44	4.72	15.56	15.61
2 *p*-Phenanthroline					10.94	10.91
3 6-6′-Diquinolyl	84.38	84.58	4.69	4.96	15.56	15.74
4 *p*-Phenanthroline	80.00	79.85	4.44	4.49	15.56	15.31
5 *p*-Phenanthroline	80.00	80.12	4.44	4.66	15.56	15.76
6 6-Chloroquinoline picrate	45.86	46.06	2.29	2.53	14.27	14.03
7 10-Hydroxy-*m*-phenanthroline	73.47	73.63	4.08	4.43	14.29	14.02

TABLE III

DERIVATIVES OF 10-HYDROXY-*m*-PHENANTHROLINE

	Formula	Properties	Water of crystallization Calcd.	Found	Analysis Calcd.	Found
Sulfate	$C_{12}H_8ON_2, H_2SO_4$	Yellow needles from alc., m. p. 273° (dec.); easily sol. in water				
Chloroplatinate	$[C_{12}H_8ON_2(HCl)_2]PtCl_4 \cdot 1^1/_2H_2O$	Yellow needles from dil. HCl, m. p. 309°	4.27	4.28	C, 23.76 H, 1.65 Pt, 32.21	C. 23.92 H, 2.04 Pt, 31.21
Picrate	$C_{12}H_8ON_2 \cdot C_6H_3O_7N_3$	Yellow needles from alc., m. p. 237° (dec.)			N, 16.47	N, 16.75

I desire to express my best thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

1. It has been reported that in the Skraup reaction with azo compounds, the presence of arsenic acid gives better results.

2. In connection with this fact, the following quinoline compounds have been prepared; quinoline, *p*-phenanthroline, 6,6′-diquinolyl, 6-chloroquinoline and 10-hydroxy-*m*-phenanthroline, of which the last is a new compound.

TOKYO, JAPAN