TABLE II

NEW KETONES

Ketone	Yield, %	M.p., °C.	B.p., °C.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	76		215–217	0.8	89.41	89.35	5.63	5.45
IV	85	83	233–234	1.5	89.41	89.30	5.63	5.66
VII	78		285–287	1.5	90.30	90.15	5.41	5.43
IX	57	120.5–121.5	251–252	0.1	90.30	90.55	5.41	5.33
XI	97	99–100	277–279	1.0	90.30	89.98	5.41	5.17
XIII	55	98–98.5	285–289	1.0	90.30	90.59	5.41	5.42

The other alumina cyclizations were carried out using essentially the same procedure and the results are summarized in Table III.

TABLE III

Ketone	Yield of product, % Aromatic cyclodehydration	Elbs-type	Temp., °C.	Time, hr.
I	4 (II)	49 (III)	240–270	2.5
IV	45 (V)	11 (VI)	260–270	2.0
VII	57 (VIII)	.....	260–280	1.5
IX	47 (X)	.....	260–270	1.5
XI	52 (XII)	.....	280–290	2.0
XIII	34 (XIV)	.....	290–300	2.5

TABLE IV

NEW HYDROCARBONS[a,b]

Hydrocarbon	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
II	160–161	94.70	94.27	5.30	5.68
V	200	94.70	94.26	5.30	5.43
VIII	190	94.87	94.80	5.13	5.24
X	153	94.87	94.72	5.13	5.27
XII	174–175	94.87	94.67	5.13	5.23
XIV	210–211	94.87	94.33	5.13	5.48

[a] Hydrocarbon VI was first prepared by E. Clar and D. Stewart, *J. Chem. Soc.*, 687 (1951). Hydrocarbon III was first prepared by F. A. Vingiello, A. Bořkovec and J. Shulman, ref. 4. [b] The ultraviolet spectra of all new hydrocarbons were taken with a Beckman spectrophotometer (model DU, 1-cm. silica cell) using 95% ethanol as the solvent. The wave length maxima (λ, mμ) for the hydrocarbons are: II and V (concn. 5 mg./l. from 210–300 mμ and 10 mg./l. from 300–390): II, 223, 250, 256, 285, 330, 347, 365, 385; V, 226, 254, 332, 348, 356, 387. All the other spectra were taken at a concn. of 10 mg./l.: VIII, 224, 260, 272, 281, 292, 319, 337, 390; X, 224, 228, 258, 271, 280, 290, 324, 335, 352, 363, 390; XII, 224, 228, 258, 272, 282, 293, 318, 337, 353, 369, 392; XIV, 224, 260, 270, 281, 292, 320, 337, 371, 390.

10-(1-Naphthyl)-1,2-benzanthracene (VIII).—A mixture of 2.0 g. of 2-(naphthylmethyl)-phenyl 1-naphthyl ketone (VII), 30 ml. of glacial acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for eight hours at 180°. The black solid which formed was separated, dissolved in benzene and washed with water. The solution was concentrated and poured into a column[14] packed with alumina and eluted with a mixture of benzene–petroleum ether (1:5). The percolate was concentrated and the hydrocarbon crystallized; yield 1.3 g. (68%), m.p. 186°. Four recrystallizations from benzene–ethanol (1:3) raised the m.p. to 190° (see Table IV for analytical data).

The other acid cyclizations were carried out using essentially the same procedure and the results are summarized in Table V.

TABLE V

Ketone	Yield of product, % Aromatic cyclodehydration	Elbs-type
I	45 (II)	36 (III)
IV	89 (V)	.....
VII	68 (VIII)	.....
IX	61 (X)	.....
XI	95 (XII)	.....
XIII	.....	48 (XIII)

BLACKSBURG, VIRGINIA

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Replacement of Bromine by Chlorine in Aromatic Compounds

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The reaction of cuprous chloride with 2-acetylamino-3-bromoanthraquinone to give the corresponding chloro compound is reported. A side reaction resulting in elimination of halogen is discussed and means of preventing it are demonstrated. The halogen exchange reaction is shown to be applicable to aromatic compounds.

2-Acetylamino-3-chloroanthraquinone is an intermediate for an important solubilized vat dye.[1] Since the established process[2] for this intermediate involves five steps from 4′-chloro-*o*-benzoylbenzoic acid some alternate methods of synthesis were considered. In contrast to chlorination the bromination of 2-aminoanthraquinone results in a high yield of 2-amino-3-bromoanthraquinone which can be acetylated without isolation.[3] Accordingly, we considered it of interest to examine procedures for the conversion of the bromo derivative to the corresponding chloro compound.

Little work has been reported on the replacement of bromine by chlorine in aromatic compounds[4–7] and in no case has such a reaction been carried out in the anthraquinone series. The drastic conditions employed and the low yields ob-

(1) The product referred to is the tetrasulfuric ester of leuco dichloroindanthrene. See K. Venkataraman, "Chemistry of Synthetic Dyes," Vol. II, Academic Press, Inc., New York, N. Y., 1952, p. 1049.

(2) P. B. Report L 25624, Frames 908–915, "Bibliography of Scientific and Industrial Reports," 8 (No. 4): 288, 290 (January 23, 1948).

(3) P. B. Report L 70341, Frame 14178, "Bibliography of Scientific and Industrial Reports," 9 (No. 3): 197 (April 16, 1948).

(4) A. Seyewetz and P. Trowitz, *Compt. rend.*, **136**, 242 (1903).

(5) J. Schmidt and G. Ladner, *Ber.*, **37**, 4402 (1904).

(6) J. Schmidt and H. Wagner, *Ann.*, **387**, 164 (1912).

tained made reported reactions of no interest for application to the compound in question.

Because of the known activating influence of cuprous ion on aromatic halogen compounds,[7] cuprous chloride was considered an ideal reagent for use in the exchange reaction. Heating 2-acetylamino-3-bromoanthraquinone with cuprous chloride in about 20 parts of α-picoline resulted in essentially quantitative conversion to the chloro compound.[8] α-Picoline was chosen as the solvent because of its known tendency to complex cuprous ion and because it could be used for the next step of the process without isolation of the resulting 2-acetylamino-3-chloroanthraquinone.[1]

The importance of the complexing effect of α-picoline was demonstrated by the fact that only an 8% yield was obtained in chlorobenzene. The addition of such diverse reagents as methyltriethylammonium chloride, dimethylformamide or dimethylcyanamide to the chlorobenzene reactions resulted in excellent yields. The complexing action of these reagents toward cuprous ion explains their effect of promoting the reaction. In the case of the quaternary ammonium salt the anion is the complexing agent.

Reduction of the α-picoline usage to about 10 parts afforded a crude product in theoretical yield which was found to contain about 85 mole per cent. of 2-acetylamino-3-chloroanthraquinone, 6 mole per cent. of 2-acetylamino-3-bromoanthraquinone and 9 mole per cent. of a halogen-free anthraquinone. Halogen elimination was thus more pronounced in concentrated solutions.

The elimination of halogen was also greatly increased in the presence of metallic copper which is an impurity in cuprous chloride. When copper, 2-acetylamino-3-bromoanthraquinone and α-picoline were heated together, a product analyzing correctly for 2-acetylamino-3-hydroxyanthraquinone was found to be present after extraction with strong alkali. While the amount of 2-acetylamino-3-hydroxyanthraquinone isolated is not sufficient to account for all of the halogen eliminated,[9] it does suggest that part of the elimination of halogen may be accounted for by the formula scheme shown. In support of this mechanism it was shown that 2-amino-3-bromoanthraquinone undergoes very little halogen elimination when heated with copper in α-picoline. It also was shown that water is not responsible for the formation of the halogen-eliminated product through hydrolysis.

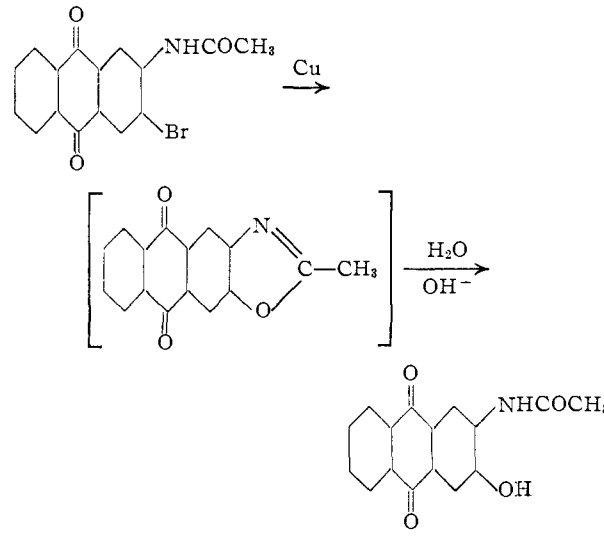
Cupric chloride was added to the reaction mixture on the assumption that it would remove metallic copper.[10] The predicted result was obtained in that the elimination reaction was avoided and the exchange reaction was nearly quantitative. It is possible that the known effect (see experiments 1 and 2, Table I) of chloride ion on the acceleration of the exchange reaction also aids in minimizing the elimination reaction in this instance.

(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(8) W. B. Hardy and R. B. Fortenbaugh, U. S. Patent 2,769,815.

(9) By-products of the dianthraquinonyl type, formed by an Ullmann reaction, probably also result from the action of the metallic copper.

(10) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 169.



The action of cuprous chloride on a few aromatic bromo compounds in α-picoline was investigated and the results are summarized in Table II. No effort was made to determine optimum conditions, but it is believed that study of each compound would probably result in a satisfactory process. Attention is directed to the much greater activity of 1-bromonaphthalene as compared with 2-bromonaphthalene in the exchange reaction.

Experimental

Reagents.—Dry, distilled solvents were used in all cases unless otherwise specified. The cuprous chloride was prepared following the procedure of reference 11. It was found that washing with ether or acetone gave a superior product. Analysis indicated about 2% metallic copper to be present.

Method of Analysis.—The mole % of chloro and bromo compounds present in the reaction mixtures was determined by elementary microanalysis for percentage of chlorine and bromine. Any difference between the sum of these mole percentages and 100 was assumed to be the percentage of the compound which had undergone halogen elimination.

Halogen Exchange Reaction of 2-Acetylamino-3-bromoanthraquinone in α-Picoline.—α-Picoline (200 cc.), 6.6 g. (0.033 mole) of cuprous chloride and 10.0 g. (0.029 mole) of 2-acetylamino-3-bromoanthraquinone[3] were stirred and heated at 130° for 8 hours. The cooled reaction mixture was poured onto ice and water and made acid to congo red by the addition of concentrated hydrochloric acid. The solid was removed by filtration and washed with water and with dilute aqueous ammonia. The yield was 8.7 (100%). The melting point of products obtained in this manner ranged from 250–255° (uncor.).

Anal. Calcd. for $C_{16}H_{10}ClNO_3$: Cl, 11.84. Found: Cl, 11.0; Br, 1.19.

It is calculated from the halogen analyses that the product contains 93 mole % 2-acetylamino-3-chloroanthraquinone, 5 mole % 2-acetylamino-3-bromoanthraquinone and 2 mole % of a halogen-free anthraquinone compound. In a run with a lower picoline usage (100 cc.) the product contained 86 mole % chloro compound, 1.6 mole % bromo compound and 12 mole % halogen-free product.

Characteristics of Halogen Elimination Reaction.—The addition of 1 g. (0.016 atom) of electrolytic copper to an experiment conducted in 100 cc. of α-picoline as outlined above gave the following results. A 19.0-g. (0.055 mole) sample of 2-acetylamino-3-bromoanthraquinone gave 15.7 g. of product, or 95% of the theoretical quantity. *Anal.* Cl, 8.45; Br, 0.81. Therefore, the mole % chloro compound is 71.5 and the mole % bromo compound is 3.5 with the halogen-free product being 25 mole %. When 1.5 g. (0.011

(11) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, second edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

TABLE I

INFLUENCE OF COMPLEXING AGENTS ON HALOGEN EXCHANGE

Expt.	Complexing agent: Kind	Mole	Reaction time, hr.	Reaction temp., °C.	Crude[d] yield, %	Product: Mole % chloro cmpd.	Mole % bromo cmpd.
1	Methyltriethylammonium chloride[a]	0.085	4	130	98	79	20
2	Dimethyl formamide[b]	.07	18	130	98	97	1
3	Dimethyl cyanamide[c]	.14	20	110	69	97	1
4	Triethylamine	.07	20	100	99	41	43
5	None		19	155	103	49	55
6	None		4	130	100	8	91

[a] Prepared by treating equimolar amounts of triethylamine and methyl chloride in *o*-dichlorobenzene for 18 hours at 25–30°. The white solid was filtered, washed with benzene and vacuum dried over paraffin. [b] Commercial material used without purification. [c] Experimental sample, American Cyanamid Co. [d] Real yields may be calculated by multiplying crude yield by mole % chloro compound.

TABLE II

EXCHANGE REACTIONS WITH OTHER BROMOAROMATIC COMPOUNDS

Expt.	Compound: Name	Mole	Mole cuprous chloride	Time, hr.	Temp., °C.	Product: Crude yield, %	Mole % chloro compound	Mole % bromo compound
1	Bromobenzene[a]	0.153	0.30	20	200	23	86	12
2	1-Bromonaphthalene[b]	.048	.20	24	130	99	71	29
3	2-Bromonaphthalene[c]	.024	.10	22	130	76	16	81
4	1,3-Dibromo-2-aminoanthraquinone[d]	.0158	.06	66	100	100	65	35
5	Bz-1-bromobenzanthrone[e]	.029	.09	72	130	91	85	12
6	1,3-Dibromoanthraquinone[f]	.03	.12	40	130	91	43	34
7	1-Amino-3-bromoanthraquinone[g]	.0167	.05	24	130	110	34	54

[a] Eastman Kodak Co. [b] Eastman Kodak Co.; redistilled, b.p. 277–279°. [c] Prepared by procedure of C. Liebermann and Fr. Palm, *Ann.*, **183**, 268 (1876); m.p. 68°. [d] Prepared from 2-aminoanthraquinone by procedure of R. Scholl, *Ber.*, **40**, 1701 (1907); m.p. 238–240°. [e] Recrystallized plant material, m.p. 169–171°. [f] Prepared from 1,3-dibromo-2-aminoanthraquinone by procedure of F. Ullmann and O. Eiser, *Ber.*, **49**, 2157 (1916); m.p. 209–210°. [g] Prepared from 1,3-dibromoanthraquinone, ref. *f*; m.p. 242–244°.

mole) of anhydrous cupric chloride was used instead of metallic copper, practically no elimination of halogen resulted and the product was 99.5% pure chloro compound with the real yield being 97%.

α-Picoline (100 cc.), 9.5 g. (0.026 mole) of 2-acetylamino-3-bromoanthraquinone and 1.7 g. (0.026 atom) of copper were heated for 5 hours at 130°. The crude product, weighing 8.4 g., was wet with alcohol and extracted with 50 cc. of 20% sodium hydroxide. Acidification of the alkaline extract gave 1.0 g. of product which melted at 320° after recrystallization from *o*-dichlorobenzene. The alkali solubility and analysis indicate this product to be 2-acetylamino-3-hydroxyanthraquinone.

Anal. Calcd. for $C_{16}H_{11}NO_4$: C, 68.5; H, 3.91; N, 4.98. Found: C, 68.5; H, 3.97; N, 5.28.

Heating 2-acetylamino-3-chloroanthraquinone under these conditions also furnished an alkali-soluble compound but in a less pure state. Heating 2-amino-3-chloroanthraquinone with copper under the same conditions resulted in loss of only 5% of the chlorine.

Comparable experiments carried out under nitrogen gave no significant difference in results. Similarly, the presence of water at 1.0% concentration in an α-picoline run gave little change in the percentage conversion to chloro compound or to halogen-free product.

Influence of Complexing Agents on Halogen Exchange in 2-Acetylamino-3-bromoanthraquinone.—Reactions conducted in non-complexing solvents to demonstrate the importance of complexing agents are summarized in Table I. In expts. 1 through 5 the solvent was 200 cc. of chlorobenzene, in expt. 6, 200 cc. of nitrobenzene was used. The usage of 2-acetylamino-3-bromoanthraquinone was 0.029 mole in each of the six expts. while the usage of cuprous chloride was 0.030 mole in expts. 1 through 3 and 0.035 mole in expts. 4 through 6. Isolation was effected by filtration in expts. 1 through 5 and by steam distillation in expt. 6.

Halogen Exchange Reactions with Other Aromatic Compounds.—The exchange of bromine for chlorine in some other bromo aromatic compounds is illustrated by Table II. The general procedure used for the reaction and the isolation of products was that followed in the α-picoline experiments. The α-picoline usage varied between 200–250 cc.

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