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Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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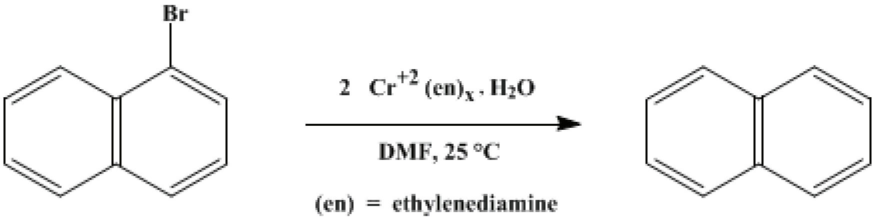
HYDROGENOLYSIS OF CARBON-HALOGEN BONDS WITH CHROMIUM(II)-EN PERCHLORATE: NAPHTHALENE FROM 1-BROMONAPHTHALENE



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Checked by Norton P. Peet and Herbert O. House.

1. Procedure

A 250-ml., three-necked flask equipped with a magnetic stirring bar, nitrogen inlet, and outlet stopcocks is charged with 60 ml. of *N,N*-dimethylformamide (Note 1) and 6.01 g. (0.100 mole) of ethylenediamine (Note 2). The outlet stopcock is connected to a trap containing mercury or Nujol, and the third neck of the flask is fitted with a rubber septum. While the solution in the flask is stirred, the system is flushed with nitrogen for 30 minutes; a static nitrogen atmosphere is maintained in the reaction vessel during the remainder of the reaction. An aqueous solution containing 0.03 mole of chromium(II) perchlorate (Note 3) is added to the reaction vessel with a hypodermic syringe, forming a purple solution of the chromium(II)-en complex. To this solution is added, with a hypodermic syringe, a solution of 1.66 g. (0.00802 mole) of 1-bromonaphthalene (Note 4) in 20 ml. of oxygen-free (Note 5) *N,N*-dimethylformamide (Note 1). The reaction solution is stirred for 70 minutes (Note 6), during which time the color changes from purple to deep red, and poured into a solution of 40 g. of ammonium sulfate in 400 ml. of 0.4 *M* hydrochloric acid. The resulting emulsion is extracted with five 60-ml. portions of diethyl ether. The combined ethereal extracts are washed with two 25-ml. portions of water, dried over potassium carbonate, and concentrated. The residue crystallizes, yielding 0.96–1.00 g. (93–98%) of naphthalene, m.p. 77–80°. Recrystallization from ethanol affords pure naphthalene as white plates, m.p. 80–81°.

2. Notes

1. Baker reagent grade *N,N*-dimethylformamide was used without purification.
2. The submitters employed, without purification, 98% ethylenediamine obtained from Mallinckrodt Chemical Works; the checkers employed material from Eastman Organic Chemicals, which was redistilled (b.p. 117–118°) before use. The amount of ethylenediamine employed is sufficient to provide three equivalents of diamine for each mole of chromium(II) and to neutralize any acid remaining in the chromium(II) perchlorate solution.
3. The submitters employed a 1.64 *M* solution of chromium(II) perchlorate, prepared by stirring a mixture of 5.7 g. of pure chromium metal pellets (United Mineral and Chemical Corporation, 129 Hudson St., New York, 10013) with 60 ml. of 20% perchloric acid under a nitrogen atmosphere at 30° for 12 hours.[2,3] The rate of dissolution of the chromium metal is increased if the metal is washed successively with concentrated hydrochloric acid and water just before it is added to the perchloric acid. The checkers employed a 0.519 *M* solution of chromium(II) perchlorate, prepared in a comparable manner with chromium metal obtained from the Mining and Metals Division, Union Carbide Corporation. The deep-blue solution of chromium(II) perchlorate is transferred to a storage vessel with a siphon or a hypodermic syringe, and the solution is stored under a nitrogen atmosphere in a vessel fitted with a rubber septum. Provided this solution is protected from oxygen, it is stable for long periods of time; aliquots for standardization or reaction are conveniently removed with a hypodermic syringe. The solution is standardized by adding 5.00-ml. aliquots to excess 1 *M* iron(III) chloride followed by

titration of the iron(II) ion produced with standard cerium(IV) sulfate solution, using phenanthroline as an indicator. [*Org. Synth.*, **Coll. Vol. 5**, 993 (1973)]. The submitters had recommended use of only slightly more [2.3 moles of chromium(II) complex per mole of halide] than the stoichiometric amount of chromium(II) complex in this reduction. However, because these concentrations of reagents lead to a very slow reaction rate in the last 5–10% of the reduction (Note 6), the checkers found it more convenient to employ excess reducing agent [3.8 moles of chromium(II) complex per mole of halide].

4. 1-Bromonaphthalene, m.p. 2–4°, obtained either from the Aldrich Chemical Company, Inc., or from Matheson, Coleman and Bell was used without further purification.

5. A slow stream of nitrogen was passed through the *N,N*-dimethylformamide for 30 minutes to remove any dissolved oxygen.

6. The progress of this reaction may be followed by quenching aliquots of the reaction solution in acidic aqueous ammonium sulfate followed by extraction with ether and analysis of the ethereal extract by GC. With a 1.2-m. GC column packed with silicone fluid, No. 710, on Chromosorb P and heated to 215°, the retention times of naphthalene and 1-bromonaphthalene were 1.9 minutes and 6.7 minutes, respectively. The submitters employed a 30-cm. GC column packed with Porpak P for this analysis. Since the presence of even 5–10% of unchanged 1-bromonaphthalene makes purification of the naphthalene difficult, it is important that the reduction be complete before the product is isolated. With reaction conditions described in this preparation [0.100 mole of ethylenediamine, 0.0080 mole of 1-bromonaphthalene, 60 ml. (0.031 mole) of 0.519 *M* chromium(II) perchlorate, and 80 ml. of *N,N*-dimethylformamide], the checkers found that reduction was usually complete in less than 15 minutes. Under the conditions [0.032 mole of ethylenediamine, 0.0040 mole of 1-bromonaphthalene, 5.5 ml. (0.0090 mole) of 1.64 *M* chromium(II) perchlorate, and 40 ml. of *N,N*-dimethylformamide] originally suggested by the submitters, a reduction time of approximately 3 hours was required for complete reduction.

3. Discussion

1-Bromonaphthalene has been reduced to naphthalene in good yield by hydrogenation over Raney nickel in methanolic potassium hydroxide,[4] by triphenyltin hydride in benzene,[5] by magnesium in 2-propanol,[6] by sodium hydrazide and hydrazine in ether,[7] and by copper(I) acetate in pyridine.[8]

The present procedure illustrates the ease of reduction of aryl, vinyl, and primary alkyl halides to the corresponding hydrocarbons with the chromium(II)-en reagent.[9] This reagent will also convert epoxides and aliphatic halides, with good leaving groups in the β-position, to olefins.[9] Although the reduction of alkyl halides with this en complex is chemically similar to reductions with solutions of other chromium(II) salts in aqueous *N,N*-dimethylformamide,[10,11] the en complexes of the chromium(II) ion are more reactive than the aquated chromium(II) ion.[9] The checkers have found that the potential measured between platinum and calomel electrodes in a solution of chromium(II) perchlorate in aqueous *N,N*-dimethylformamide is increased by the addition of ethylenediamine until three equivalents of the diamine have been added. However, presumably at least one of the six coordination sites on the chromium(II) ion must be vacant at the time reduction of a halide occurs, permitting transfer of the halogen atom from the substrate to the chromium ion.[9]

Chromium(II) perchlorate is the salt of choice for preparing the en complex in *N,N*-dimethylformamide. At comparable concentrations chromium(II) sulfate[10] is insoluble, and chromium (II) chloride[2,11] is only partially soluble in the reaction solution.

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

methanolic potassium hydroxide

CHROMIUM(II)-EN PERCHLORATE

chromium(II)-en complex

chromium(II) complex

ethanol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

magnesium (7439-95-4)

oxygen (7782-44-7)

nitrogen (7727-37-9)

Raney nickel (7440-02-0)

pyridine (110-86-1)

2-propanol (67-63-0)

1-bromonaphthalene (90-11-9)

Naphthalene (91-20-3)

iron(III) chloride (7705-08-0)

ammonium sulfate (7783-20-2)

hydrazine (302-01-2)

chromium (7440-47-3)

N,N-dimethylformamide (68-12-2)

ethylenediamine (107-15-3)

chromium(II) chloride (10049-05-5)

cerium(IV) sulfate (13590-82-4)

CHROMIUM(II) SULFATE

chromium(II)

perchloric acid (7601-90-3)

phenanthroline

chromium(II) perchlorate

iron(II) ion

triphenyltin hydride (892-20-6)

sodium hydrazide

copper(I) acetate (598-54-9)