aldehyde was treated with concentrated aqueous ammonia, or with ammonium chloride, ammonium acetate or acetamide in the presence of Triton B. The elemental analysis of the resin did not correspond to the condensation of nitromalonaldehyde with ammonia in a simple ratio. No significant characteristics were obtained in the infrared, visible or ultraviolet absorption spectra of the resin.

Unsuccessful Procedures for the Reduction of 2-Nitro-5-phenylpyrimidine.[25]—The following procedures gave either no reaction or intractable products: tin and hydrochloric acid,[26] hydrazine hydrate and Raney nickel,[27] stannous chloride and hydrochloric acid[28] or platinum oxide catalyst and hydrogen at several atmospheres pressure.

Reduction with Sodium Hydrosulfite.—A suspension of 0.20 g. of 2-nitro-5-phenylpyrimidine in a solution of 0.40 g. of sodium hydroxide in 10 ml. of water was warmed and stirred while 1.05 g. of sodium hydrosulfite was added. The solution was centrifuged to remove a small amount of brown solid, then cooled to 5° and treated with 2 ml. of acetic anhydride. White crystals of 5-acetylamino-2-phenylpyrimidine were formed which were recrystallized from 20% alcohol–water to give shiny, white platelets, m.p. 208–209°.

Anal. Calcd. for $C_{12}H_{11}N_3O$: N, 19.71. Found: N, 19.60.

Hydrogenation with Palladium Catalyst.—A suspension of 2.00 g. (0.01 mole) of 5-nitro-2-phenylpyrimidine in 200 ml. of absolute ethanol was shaken with 0.6 g. of 5% palladium-on-charcoal catalyst at room temperature for one-half hour under a hydrogen pressure of three atmospheres. The suspension was evaporated to dryness *in vacuo* on the steam-bath and the residue was extracted with boiling benzene. Filtration and cooling gave feathery, white clusters and a second crop was obtained by concentration of the liquor. The yield was 1.50 g. (88%) of 5-amino-2-phenyl-pyrimidine melting at 90.5–92°; previously reported[13] 90–91°.

5-Amino-2-*p*-tolylpyrimidine, m.p. 183.5–184° (sealed capillary), was obtained in 95% yield by the use of the same reduction procedure on the corresponding nitro compound.

Anal. Calcd. for $C_{11}H_{11}N_3$: C, 71.35; H, 5.95. Found: C, 70.98; H, 6.18.

Attempted reductions of 2-(4-chlorophenyl)-, 2-(4-bromophenyl)- and 2-(4-methoxyphenyl)-pyrimidines under the same conditions were not successful. At high pressure or at elevated temperatures oily or tarry products were obtained.

Attempted Diazotization of 5-Amino-2-phenylpyrimidine.—The following reaction conditions were tried: sodium nitrite in aqueous hydrochloric acid, nitrosylsulfuric acid in sulfuric acid,[29] bromine and sodium nitrite in hydrobromic acid,[30] isoamyl nitrite and hydrogen chloride in absolute ethanol, and sodium nitrite in aqueous trifluoroacetic acid.[31] Each reaction mixture was tested for the presence of aromatic diazonium salt by adding it to an alkaline solution of β-naphthol. In no case was a color observed which could be attributed to the formation of a coupling product.

Biological Testing.—Some of the compounds described in this publication were submitted to a microbiological screening program with emphasis on pyrimidine antimetabolite activity under the supervision of Dr. Irving Slotnick, Roswell Park Memorial Institute, Buffalo 3, N. Y.

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[25] Raney nickel at low hydrogen pressure in dioxane has previously been reported to result in the formation of 2,2'-diphenyl-5,5'-azoxypyrimidine, P. E. Fanta and T. R. Hughes, THIS JOURNAL, **72**, 5343 (1950).

[26] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York N. Y., 1948, p. 144.

[27] D. Balcom and A. Furst, THIS JOURNAL, **75**, 4334 (1953).

[28] L. A. Perez-Medina, R. P. Mariella and S. M. McElvain, *ibid.*, **69**, 2574 (1947).

[29] H. A. J. Schoutissen, *ibid.*, **55**, 4531 (1933).

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[31] M. R. Pettit, M. Stacey and J. C. Tatlow, *J. Chem. Soc.*, 3081 (1953).

CHICAGO 16, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Formation of Naphthalenes from Indenes. II[1,2]

BY WILLIAM E. PARHAM, HARRY E. REIFF[3] AND PAUL SWARTZENTRUBER

RECEIVED AUGUST 22, 1955

The yield of 2-chloronaphthalene from indene and chloroform has been increased to 65% by utilization of potassium *t*-butoxide as the base for generation of dichlorocarbene from chloroform. The proposed intermediate, 1,1-dichloro-1a,6a-dihydrocycloprop[a]indene (I), has been isolated. The status of this intermediate in the ring expansion reaction has been confirmed by its quantitative conversion into 2-chloronaphthalene, a reaction which appears to follow first-order kinetics in neutral or basic media. The reaction of indene, potassium *t*-butoxide and bromoform affords a 51% yield of 2-bromonaphthalene. A similar reaction, using iodoform, does not lead to the formation of iodonaphthalene; the iodoform is reduced to methylene iodide. The reaction of 1-(or 3)-methylindene with potassium *t*-butoxide and bromoform leads to the formation of 1-methyl-2-bromonaphthalene in 44% yield. No evidence for the formation of the 3-bromoisomer was obtained.

A new synthesis of 2-chloronaphthalene was recently described[1] which involves the reaction of indenylsodium with chloroform in excess indene. This paper describes additional studies of this, and related, reactions.

2-Chloronaphthalene and an azulene were the only isolable compounds[1] when the crude reaction mixture obtained from indenylsodium, chloroform and indene was distilled with steam. It has been found in this study, however, that 2-chloronaphthalene is not present when only non-polar solvents are employed in processing the crude reaction mixture. In this case the principal product (2–4% yield) is a neutral compound which has been assigned the structure 1,1-dichloro-1a,6a-dihydrocycloprop[a]indene (I). Analysis and molecular weight determinations establish the empirical formula $C_{10}H_8Cl_2$ for the neutral compound. The substance gives no immediate reaction with bromine in carbon tetrachloride or with neutral potassium permanganate solution, indicating the absence of an olefinic bond. The ultraviolet spectrum of the material is quite similar to that of indane, and, specifically, absorption in the region of 250 mμ, typical of a double bond conjugated with an aromatic system,[4] is absent. These data, together with the report of Doering and Hoffmann[5] that olefins such as cyclo-

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[1] Preceding paper: W. E. Parham and H. E. Reiff, THIS JOURNAL, **77**, 1177 (1955).

[2] Presented in part at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.

[3] National Science Foundation Pre-doctoral Fellow, 1954–1955.

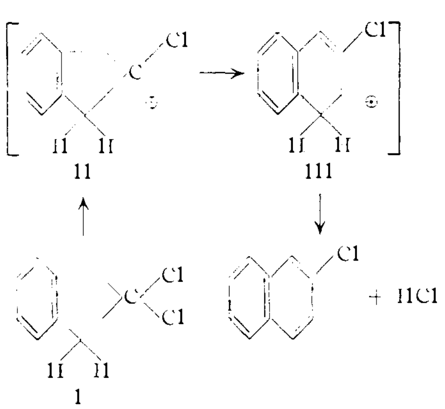
[4] T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947).

[5] W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

hexene and butene-2 react with chloroform and base to give derivatives of 1,1-dichlorocyclopropane, establish the structure I for this compound.

The cyclopropyl derivative I has been shown to be an intermediate in the ring expansion reaction by its facile conversion to 2-chloronaphthalene. This reaction is essentially quantitative and occurs rapidly in polar solvents such as ethanol–water, but more slowly in indene or in the solid state.

The conversion of I into 2-chloronaphthalene and hydrogen chloride has been found, by preliminary rate studies, to follow first-order kinetics in 80% ethanol; the rate being dependent only upon the concentration of I. The reaction also appears to be first order in the presence of one or two molar equivalents of sodium hydroxide—the rate again dependent only upon the concentration of I. There is a primary, positive salt effect as shown by the effect of the addition of sodium perchlorate on the rate constant. The pertinent rate data are found in the experimental section of this report. These results indicate that the rate-determining step in this reaction is not primarily ionization of a proton, but rather of chloride ion.[6]



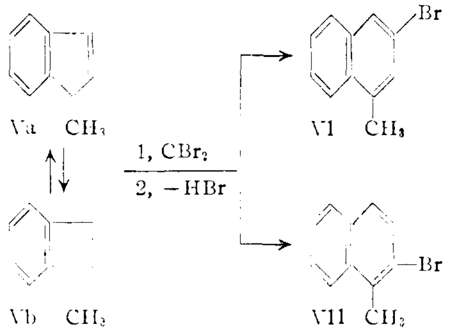
Since 2-chloronaphthalene was not found in the reaction mixture from which the cyclopropyl compound I was isolated, it appeared that the indene anion functioned solely as a base for the generation of dichlorobene from chloroform, and was not a required reactant in the formation of I. Potassium hydroxide in acetal proved to be ineffective; however, the use of potassium *t*-butoxide, the base most successfully employed by Doering and Hoffmann in their reaction involving olefins and chloroform,[5] resulted in yields of 65–70% of I, and subsequently a 65% over-all yield of 2-chloronaphthalene.

Attempts to extend this ring expansion reaction to cyclopentadiene have so far been unsuccessful. No evidence for the formation of chlorobenzene has been obtained when the reaction was carried out with potassium *t*-butoxide using excess cyclopentadiene or petroleum ether as solvent. The principal non-tarry product appears to be primarily dimer, or perhaps higher polymers, of cyclopentadiene.

The reaction of indene, bromoform and potassium *t*-butoxide, using indene as the solvent, has been examined. The same conditions were employed as for the related reaction with chloroform, and the reaction mixture was processed by steam distillation. A 51% yield of pure 2-bromonaphthalene, identical with authentic material, was obtained.[7]

The reaction of iodoform with potassium *t*-butoxide and indene does not follow the course observed for chloroform and bromoform; the presence of 2-iodonaphthalene has not been demonstrated. An inordinately large quantity of tars are formed, and these tars give only faintly positive Beilstein test for halogen. The bulk of the halogen-containing organic material is contained in the recovered indene fraction and has been identified as methylene iodide (b.p. 180–181°, b.p. of indene 181–182°) by its conversion into the corresponding picrate of methylene-bis-isothiouronium dihydroiodide. Comparison of the infrared spectra of synthetic mixtures of methylene iodide and indene and the refractive indices of such mixtures to the indene distillate indicates that a minimum of 46% of the theoretical amount of methylene iodide is present. The formation of methylene iodide from iodoform under the basic conditions of the reaction is not unusual. A similar reaction in the presence of sodium ethoxide[8] in ethanol, and sodium acetate[9] in ethanol, has been reported. The mechanism of the reaction is not known.

A study of the reaction of bromoform, base and 1- (or 3)-methylindene has been made in order to test the applicability of this ring expansion reaction to the synthesis of naphthalenes disubstituted in one ring. 1-Methylindene (Va) may exist in the form of its tautomer, 3-methylindene (Vb), and consequently two possible methylbromonaphthalenes could result. One would anticipate that 3-methylindene would be the predominate isomer, and thus VII the principal product; consequently, a secondary objective in this study was to ascertain whether or not steric selectivity is an important factor in the reaction of such tautomers with dibromocarbene. If such were the case, then significant quantities of VI would be expected.



The reaction was carried out in the usual way with potassium *t*-butoxide, 1- (or 3)-methylindene and bromoform, and the product was processed by steam distillation and chromatography. A 61%

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(6) The probable concerted rearrangement of II to III makes comparison of the chemical behavior of I to similar 1,1-dichlorocyclopropanes infeasible. Thus, the markedly less reactivity shown by dichlorocyclopropanes, in general, is not necessarily pertinent.

(7) An azulene was also apparently formed in the reaction, as evidenced by the blue color of the steam distillate; however, no attempt was made to isolate this product since previous work with chloroform indicated that the azulene is formed in very low yield.

(8) A. Butlerow, *Ann. chim. phys.*, [3] **53**, 313 (1858).

(9) S. Bagnara, *Eng. Mining J. Press*, **116**, 51 (1923).

yield of methylbromonaphthalene was obtained that melted at 26–29°; however, this was not pure and contained small amounts of methylindene. 1-Methyl-2-bromonaphthalene (VII) melts at 32–33°, and the isomer VI melts at 46–47°. The crude methylbromonaphthalene was recrystallized from ethanol and the mother liquors were rechromatographed. A 44% yield of pure 1-methyl-2-bromonaphthalene (VII) was easily obtained; there was no evidence for the presence of the isomer VI.

Studies of the reactions of indenes with base and carbene precursors are being continued.

Experimental

1,1-Dichloro-1a,6a-dihydrocycloprop[α]indene (I).—All reactions were carried out in an atmosphere of nitrogen.

Potassium *t*-butoxide was prepared from potassium (13.3 g.) as described by Doering and Hoffmann.[5] The caked salt was powdered manually, and 345 g. of purified indene was added. The cold (0°), stirred mixture was treated dropwise (12 min.) with 40 g. (0.33 mole) of chloroform, and the resulting mixture was stirred for one hour and then added to 300 ml. of petroleum ether. The filtered petroleum ether extract was concentrated and indene (252 g., $n^{25}\text{D}$ 1.5735) was removed by distillation through a 12-inch helices-packed column (0.6 mm., pot temperature not exceeding 50°).[10] The solid residue was dissolved in 600 ml. of petroleum ether and chromatographed using 600 g. of Merck alumina. Fraction 1 was obtained using petroleum ether (1.5 l.), and was blue in color. Fraction 2 was obtained using benzene (20%)-petroleum ether (80%).

The two fractions were processed in the following way: the solvent was removed and the resulting solid was recrystallized from petroleum ether (b.p. 28–38°). Solvent was removed from the mother liquors and more indene was removed.[10] The cycle was repeated. The total weight of indene recovered was 290 g.; the total weight of I (m.p. 72–75°) was 47.5 g. (71.5%). Further purification of I was achieved by recrystallization from ethanol (43 g., 65%, m.p. 75–76°).

Anal. Calcd. for $C_{10}H_8Cl_2$: C, 60.33; H, 4.05; Cl, 35.62; mol. wt., 199.1. Found: C, 60.53; H, 4.06; Cl, 35.42; mol. wt. (Rast), 182, 187.

This compound did not react immediately with bromine in carbon tetrachloride or with neutral potassium permanganate solution. The ultraviolet spectrum was run in 95% ethanol, and showed maxima and minima as follows: λ_{max}^{264} (log ϵ 2.88), λ_{max}^{270} (log ϵ 3.08), λ_{max}^{277} (log ϵ 3.19); λ_{min}^{247} (log ϵ 2.38), λ_{min}^{266} (log ϵ 2.86), λ_{min}^{274} (log ϵ 2.66), λ_{min} (log ϵ <2.0).

In another experiment, in which 0.10 mole of chloroform was employed, the reaction mixture was quenched on ice and then distilled with steam. The distillate was extracted with ether, dried and indene was removed as described above. The residue was treated with absolute ethanol and filtered to remove insoluble material (probably indene polymer). Solid potassium hydroxide (about 1 g.) was added, and the resulting solution was heated at the reflux temperature for two hours. The ethanol solution was concentrated to 40 ml. and organic material was precipitated by the addition of excess water. The dark brown material was dissolved in ethanol, treated with charcoal and fractionally crystallized to give 8.4 g. (52% yield) of 2-chloronaphthalene (m.p. 55–58°).

The cyclopropyl compound (I) was first isolated from reactions in which indenylsodium (prepared from indene and sodium,[1] or from indene and sodium hydride) was employed as the base. The reaction product, obtained from 0.28 mole of chloroform, was diluted with petroleum ether, filtered and processed by chromatography. 2-Chloronaphthalene was not detected as a product from such reactions. The yield of pure I was 2–4%. The azulene concentrate (200 mg.) was obtained from impure I by extraction with phosphoric acid. Attempts to further purify the azulene by sublimation resulted in considerable decomposition. The spectrum of the sublimate (29.6 mg.) has been reported.[1]

Formation of 2-Chloronaphthalene from I.—A mixture of 4.0 g. of I was dissolved in 100 ml. of absolute ethanol containing 10 g. of potassium hydroxide. The solution was refluxed on the steam-bath for four hours, then cooled in an ice-bath. Precipitated potassium chloride was removed by filtration, and the filtrate was concentrated to a volume of 30 ml. by distillation of alcohol. This residue was diluted with 100 ml. of water and cooled. The crystallized solid was removed by filtration, washed well with water and air-dried to give 3.2 g. (98% yield) of 2-chloronaphthalene, m.p. 58–59°. The yield of 2-chloronaphthalene (m.p. 58–59°) was 94% when a solution of I in ethanol-water (50:50) was heated at the reflux temperature for 24 hours.

Kinetic Studies.—The following general procedure was used: A weighed amount of 1,1-dichloro-1a,6a-dihydrocycloprop[a]indene (I) was dissolved in absolute ethanol in a 250-ml. volumetric flask. Either 50 ml. of distilled water, or a volume of standardized base plus sufficient water to equal 50 ml., was added, and the solution was made up to 250 ml. with additional ethanol. In those runs using sodium perchlorate, the weighed salt was added before addition of water.

Thirty-ml. aliquots were pipetted into each of seven 125 ml. glass-stoppered flasks which were then submerged in a bath thermostated at 50.0 ± 0.1°. After ten minutes, a sample was removed and titrated with either 0.01 *N* sodium hydroxide or 0.05 *N* hydrochloric acid, depending upon the type of run being made. All remaining aliquots were then corrected for the amount of acid or base required by the 10-minute sample. Measurements were then made at 60-min. intervals for 8 hours (33% completion).

Compn. in 80% ethanol	Integrated first-order rate constant × 10^3, min.$^{-1}$
0.05028 *M* compound I	8.43 ± 0.16
.05028 *M* compound I .05028 *M* NaOH	8.81 ± 0.25
.02676 *M* compound I .05392 *M* NaOH	9.30 ± 0.34
.05076 *M* compound I .04864 *M* NaOH .428 *M* $NaClO_4$	9.91 ± 0.29
.05024 *M* compound I .0998 *M* $NaClO_4$	9.02 ± 0.23

Reaction of Potassium *t*-Butoxide, Indene and Bromoform.—The reaction conditions, employing potassium (11.5 g.), indene (320 g.) and bromoform (70 g., 0.276 mole), were essentially identical to those described above, for the reaction with chloroform. The petroleum ether filtrate (300 ml.) was distilled with steam and the dark blue distillate was collected, washed with aqueous sodium carbonate, dried and distilled. Indene was removed (b.p. 54° (8 mm.)) until the residue was about 40 ml. This residue was diluted with petroleum ether and chromatographed on 400 g. of Merck alumina. Petroleum ether (*ca.* 2 l., b.p. 60–68°) was used to develop the column. A small forerun contained indene (6 g.). The main blue-green eluate was concentrated to give 32 g. of pale blue-green solid. Traces of indene were removed at 0.3 mm., at room temperature, and 29.6 g. of 2-bromonaphthalene (m.p. 53–55°, 51.7%) was obtained. The product melted at 55–57° after recrystallization from ethanol-water. The product caused no depression in melting point when mixed with authentic 2-bromonaphthalene (m.p. and mixed m.p. 56–57°). The picrate of the product, m.p. 81–83°, caused no depression in melting point when admixed with an authentic sample of the picrate of 2-bromonaphthalene (m.p. 81–83°).[11]

The Reaction of Potassium *t*-Butoxide, Iodoform and Indene.—This reaction was carried out using 0.203 mole of iodoform and 240 g. of indene, by a procedure similar to that described above for bromoform and chloroform. The reaction mixture was stirred for an additional five hours at 0°, quenched on ice, and distilled with steam. The light yellow distillate was extracted with ether, and the ethereal extract dried ($MgSO_4$) and fractionally distilled. A total of 235 g. of colorless liquid was obtained boiling at 56–57° (10 mm.), $n^{25}\text{D}$ 1.5815. Approximately 1.5 g. of ether-insoluble resi-

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(10) When indene is being removed, it is important to use a low temperature and an effective column. This prevents loss of product by codistillation, and also the thermal decomposition of I.

(11) N. Jefremov, *J. Russ. Phys. Chem. Soc.*, **50**, 372 (1918).

due remained. The boiling point and refractive index of the distillate suggested that it was a mixture of methylene iodide (b.p. 180–181°, $n^{24}D$ 1.7385) and indene (b.p. 181–182°, $n^{25}D$ 1.5735). This was confirmed as described below.

1. A solution of the original distillate (20 g.), 95% ethanol (40 ml.) and thiourea (4.0 g.), was heated at the reflux temperature for one hour and then cooled. Precipitated salts were separated, and the filtrate was concentrated to a volume of 25 ml. by distillation. Addition of ether to the concentrate caused the precipitation of additional solids, which were combined with that originally obtained.

The crude methylene-bis-isothiouronium dihydroiodide was recrystallized from ethanol–ether, and 1.0 g. of the salt was dissolved in water. A saturated solution of picric acid in water (40 ml.) was added and the yellow precipitate that formed was recrystallized from hot water. This product melted at 232–233° dec. and caused no depression in melting point when admixed with the product (m.p. 232–233°) obtained from authentic methylene iodide.[12] The infrared spectra of the two samples were identical.

2. A sample of 140 g. of the distillate, $n^{25}D$ 1.5815, was fractionated using a Podbielniak column, and the 15 g. forerun, $n^{25}D$ 1.6173 was redistilled using a Piros-Glover spinning band column. A 4 g. forerun of the latter distillation, b.p. 64–65° (14 mm.), $n^{25}D$ 1.6274, was collected. The refractive index of this material indicates it to be a mixture of about 65% methylene iodide and 35% indene. A synthetic mixture of 65.7% methylene iodide and 34.3% indene, $n^{25}D$ 1.6274, possessed an almost identical infrared spectrum to that of the distillate. Calculation of the quantity of methylene iodide from the refractive index, assuming an ideal, two component system, indicated a minimum of 46% of the theoretical amount to be present in the original distillate ($n^{25}D$ 1.5815).

1-(or 3)-Methylindene.[13]—The procedure of Stoermer and Laage was employed with the following modification. The reaction product obtained from 1-hydrindone[14–16] (32.0 g., 0.242 mole), in 150 ml. of ether and of methylmagnesium iodide (0.328 ml.), in 150 ml. of ether, was treated with 300 ml. of ice and 100 ml. of 20% sulfuric acid. The ether was then removed by distillation and an additional 100 ml. of 20% sulfuric acid was added. The mixture was heated at the reflux temperature for 15 minutes, and then processed by steam distillation and fractional distillation of the dry product. 1-Methylindene (19.7 g., 62% yield, $n^{25}D$ 1.5587) was collected at 76–78° (11 mm.).

Reaction of 1-(or 3)-Methylindene with Bromoform in the Presence of Potassium *t*-Butoxide.—1-(or 3)-methylindene (71.6 g., 0.551 mole) was added with stirring and cooling to potassium *t*-butoxide prepared from 3.2 g. (0.082 g. atom) of potassium metal. Freshly distilled bromoform (20.2 g., 0.080 mole) was added dropwise over a period of five minutes. The color of the mixture changed from bright red to reddish-brown. The mixture was then stirred for an additional 45 minutes, and 100 ml. of ice and 200 ml. of water was added. Aqueous sodium carbonate (60 ml. of 3 *N*) was added, and the resulting mixture was distilled with steam. The green distillate was extracted with petroleum ether and the extract was dried ($MgSO_4$) and vacuum distilled through a 10-inch column packed with glass helices. The residue obtained, after the solvent and 1-methylindene (56.6 g., $n^{25}D$ 1.5599) were removed, was a greenish-brown oil which was a solid at 0°. This material was dissolved in 75 ml. of absolute ethanol, 1 g. of potassium hydroxide was added, and the resulting mixture was heated at the reflux temperature for 30 minutes. Distillation of the ethanol left a dark brown oily residue. Petroleum ether (150 ml., b.p. 60–68°) was added and the resulting solution was heated and then filtered. The solid material was washed well with hot petroleum ether and the combined brown ether solutions were chromatographed on a column containing 250 g. of Merck alumina.

The column was eluted successively with petroleum ether (2500 ml., b.p. 60–68°), 20% benzene–petroleum ether (500 ml.), 50% benzene–petroleum ether (2500 ml.), benzene (1000 ml.), chloroform (500 ml.) and 95% ethanol (500 ml.). The petroleum ether fraction afforded a pale blue oil which was recrystallized once from petroleum ether to give 8.03 g. of pale blue solid (m.p. 27–29°). The 20% benzene fraction contained only a small amount of material. This was combined with the mother liquors described above, and the mixture was rechromatographed on 150 g. of alumina. An additional 1.80 g. of white solid (m.p. 27.5–29°) was obtained. The combined solid (9.83 g., 56%) was recrystallized from absolute ethanol and gave 7.36 g. (42%) of pure 1-methyl-2-bromonaphthalene (m.p. and mixed m.p. 31–33°).

The remaining fractions from the original chromatogram contained only small amounts of material. All residues were combined (including that obtained from the mother liquor of the ethanol crystallization) to give 1.82 g. of material. This was rechromatographed, and an additional 0.87 g. of solid (m.p. 26–29°) was obtained. An additional 0.49 g. of VII (m.p. 31–33°) was obtained by recrystallization of this product from ethanol. By these procedures a total of 10.70 g. (61%) yield of crude VII (m.p. 26–29°) was obtained which afforded 7.85 g. (44%) of pure VII.

Anal. Calcd. for $C_{11}H_9Br$: C, 59.75; H, 4.10. Found: C, 59.51; H, 4.40.

Authentic 1-methyl-2-bromonaphthalene (m.p. 31–33°) was prepared from 1-methyl-2-naphthylamine[17,18] by a procedure analogous to that described by Fenton, DeWald and Arnold.[19] The two samples of VII were identical as evidenced by their infrared spectra, melting points and mixed melting points.

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