g.c. The distillation residue, 28.6 g., was dissolved in 200 ml. of carbon tetrachloride, and the polystyrene was precipitated by the slow addition of 600 ml. of methanol. Evaporation of the filtrate gave 1.90 g. of dark brown liquid. Distillation of the liquid, b.p. 160–200° (0.1 mm.), and g.c. analysis showed the presence of at least four components. The n.m.r. spectrum of this fraction showed two multiplets centered at δ -1.2 (1.75) and -0.9 (1.00).

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Reactions of 1-(Chloromethyl)naphthalenes

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In a previous study of the reactions of methyl substituted 1,4-epoxy-1,4-dihydronaphthalenes,[1] two alkyl substituted 1-(chloromethyl)naphthalenes were obtained readily by reaction of the epoxides with dry hydrogen chloride in methanol. In view of the potential synthetic value of the (chloromethyl)naphthalenes, and also because some of their reactions appeared to be somewhat unusual, it was desired to study their behavior more fully. For this purpose three alkyl-substituted 1-(chloromethyl)naphthalenes were prepared and used, namely, 4-methyl-,[2] 2,3,4-trimethyl-,[1] and 4-methyl-2,3-diethyl-.[1] Some reactions of the second compound were reported previously.[1]

The Wurtz reaction with sodium, in octane as reaction medium, gave the expected products, one of which, 1,2-bis(4-methyl-1-naphthyl)ethane (I), had been described before.[3] *n*-Octane was chosen as solvent since its boiling temperature is high enough to liquify the sodium metal for efficient reaction. Apparently the reaction is not rapid under these conditions, since in some cases unreacted chloro compound was recovered. No attempt was made to improve the yields, but it is likely that a higher-boiling inert liquid should be more effective.

Hydrolysis of the (chloromethyl)naphthalenes failed in all cases to give the corresponding alcohols, but invariably gave the ethers. Although it has been reported[4] that 1-(hydroxymethyl)-4-methylnaphthalene was obtained in this way in very low yield together with much of the ether, we were not able to confirm this. Similarly, 1-(chloromethyl)-2,3,4-trimethylnaphthalene gave only bis(2,3,4-trimethyl-1-naphthyl methyl) ether,[1] and 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene gave a 78% yield of bis(4-methyl-2,3-diethyl-1-naphthyl methyl) ether (VI).

Displacement of the chlorine by methoxyl was readily accomplished by boiling methanol or sodium methoxide in methanol. It is interesting to note that, whereas 1-(methoxymethyl)-2,3,4-trimethylnaphthalene[1] is a solid, its homolog, 1-(methoxymethyl)-4-methyl-2,3-diethylnaphthalene (III), is a liquid which failed to solidify after cooling several hours at $-40°$. It is also worth noting that, when the chloromethyl compound is boiled with methanol containing a little aqueous hydrochloric acid, the product is the ether. Thus, 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene gave a 45% yield of the ether VI.

1-Methoxymethyl)-4-methyl-2,3-diethylnaphthalene (III) was subjected to a Zeisel methoxyl analysis[5] and the residue was worked up to see if it contained some of the alcohol. However, the product proved to be the hydrocarbon, 1,4-dimethyl-2,3-diethylnaphthalene (IV), apparently the result of complete reduction by the hydriodic acid. The identity of this product was confirmed by reducing 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene with zinc and acid to obtain the same compound (IV).

Several attempts were made to make the Grignard reagent of the (chloromethyl)naphthalenes. Success was achieved only in the case of 1-(chloromethyl)naphthalene, whose Grignard was converted to 1-naphthylacetic acid (VII).[6] It had been reported[7] that this reaction goes to 88–92% completion. In several attempts it was found impossible to obtain any Grignard reaction with the 1-(chloromethyl)naphthalenes substituted by methyl groups in the 4-, or 2-, 3-, and 4-positions, or by methyl in the 4-, and ethyl groups in the 2- and 3-positions. In ether as solvent, catalysts such as iodine, ethylene bromide, and methyl iodide were tried, but no reaction took place even after 2 hr. at reflux temperature followed by 24 hr. at room temperature. In every case the starting material was recovered nearly quantitatively.

Experimental[8]

1,2-Bis(4-methyl-1-naphthyl)ethane (I).—1-(Chloromethyl)-4-methylnaphthalene (0.400 g., m.p. 61–62°) was dissolved in 20 ml. of *n*-octane, sodium (1 g.) was added, and the mixture refluxed for 3 hr. at 110–115°. The warm mixture was filtered then thoroughly cooled at 0–10°, and the crystalline product was filtered and washed with cold hexane. The yield was 0.160 g. (50%), m.p. 154–155°, lit.[3] m.p. 152–153°. The ultraviolet spectrum in cyclohexane, λ_{max} mμ (log ϵ), showed absorption at 213 sh (4.78), 230 (5.03), 269 sh (3.87), 283 (4.11), 292.5 (4.23), 303 (4.13), and 316 (3.34); lit.[3] 228 (5.05), 292 (4.2), and 302 (4.1).

1,2-Bis(2,3,4-trimethyl-1-naphthyl)ethane (II).—1-(Chloromethyl)-2,3,4-trimethylnaphthalene[1] (0.200 g.) was dissolved in 10 ml. of *n*-octane, sodium (0.5 g.) was added, and the mixture refluxed for 4 hr. On cooling the filtered solution, the product did not crystallize. The solvent was removed under vacuum; the residue was taken up in hexane and chromatographed on a column of neutral alumina. The first fraction consisted of some starting material, while the second yielded 0.12 g. (72%) of the product, m.p. 195–200°. Recrystallization from hexane gave m.p. 207.8–209°. The ultraviolet spectrum in cyclohexane, λ_{max} mμ (log ϵ), showed absorption at 219 sh (4.82), 233 sh (5.07), 235 (5.09), 275 sh (3.88), 2.87 (4.07), 298 (4.18), 311 (4.08), and 323 (3.32).

Anal. Calcd. for $C_{28}H_{30}$ (366.5): C, 91.80; H, 8.20. Found: C, 91.67; H, 8.36.

1-(Methoxymethyl)-4-methyl-2,3-diethylnaphthalene (III).—

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1-(Chloromethyl)-4-methyl-2,3-diethylnaphthalene[1] (0.200 g.) was added to a solution of sodium (0.1 g.) in 10 ml. of absolute methanol. After refluxing for 1 hr., the mixture was filtered, the solvent was removed under vacuum, and the residue was taken up in hexane and chromatographed on neutral alumina to give 0.120 g. (60%) of an oil which did not solidify at −40°. The infrared spectrum showed a strong absorption at 1050–1100 $cm.^{-1}$.

Anal. Calcd. for $C_{17}H_{22}O$ (242.3): C, 84.29; H, 9.09; OMe, 12.8. Found: C, 84.08; H, 9.13; OMe, 11.5.

In another experiment, 1-(chloromethyl)-4-methyl-2,3-diethylnaphthalene (0.200 g.) was boiled for 5 min. with 3 ml. of methanol, the mixture was poured into water, the oil was extracted with benzene, and the latter was removed to leave the crude oily product. This oil was converted to its picrate which was placed on a column of silica gel. Pouring hexane through the column gave an eluate containing 0.12 g. (60%) of the product, identical with that obtained before.

1,4-Dimethyl-2,3-diethylnaphthalene (IV). Method A.—A 0.100-g. sample of III was boiled for 1 hr. with 58% hydriodic acid in the manner used in the usual Zeisel alkoxyl analysis.[5] After the methyl iodide had been removed and determined quantitatively, the residual solution was poured into water, the oil which separated was extracted with hexane, and the solution was clarified with carbon and then passed through a column of neutral alumina to give 0.040 g., m.p. 53.1–54°, which was not further purified. The infrared spectrum showed no hydroxyl absorption.

Method B.—1-(Chloromethyl)-4-methyl-2,3-diethylnaphthalene (0.200 g.) was dissolved in 10 ml. of glacial acetic acid, 1 ml. of concentrated hydrochloric acid was added, and then 1 g. of zinc dust. After refluxing for 2 hr., the mixture was cooled, poured into water, and the product was extracted with hexane and dried over potassium carbonate. Chromatographic separation on neutral alumina gave a fraction, 0.080 g. (46%), m.p. 56.2–57.1°, identical with that obtained by method A. The ultraviolet spectrum in ethanol, λ_{max} mμ (log ε), showed absorption at 214 (4.44), 234 (4.91), 264 sh (3.26), 274 sh (3.52), 286 (3.70), 295 (3.74), 306 sh (3.59), and 324.5 (2.75).

Anal. Calcd. for $C_{16}H_{20}$ (212.3): C, 90.56; H, 9.44. Found: C, 90.30; H, 9.83.

1,2-Bis(4-methyl-2,3-diethyl-1-naphthyl)ethane (V).—A solution of 1(chloromethyl)-4-methyl-2,3-diethylnaphthalene (0.200 g.) in 10 ml. of *n*-octane was refluxed for 4 hr. with 0.5 g. of sodium. Filtering and cooling thoroughly gave no precipitate. The solvent was removed under vacuum, and the residue was stirred with cold methanol leaving 0.080 g. (50%) of a solid, m.p. 168–170°. Purification of its hexane solution on a column of neutral alumina gave 0.050 g. of product, m.p. 175.8–176.9°. The ultraviolet spectrum in cyclohexane, λ_{max} mμ (log ε), showed absorption at 219 sh (4.76), 233 (5.01), 239 (5.09) 266 sh (3.60), 276 sh (3.82), 289 (4.02), 300 (4.13), 310 (4.03), and 324 (3.37).

Anal. Calcd. for $C_{32}H_{38}$ (422.6): C, 90.99; H, 9.01. Found: C, 90.44; H, 9.69.

Bis(4-methyl-2,3-diethyl-1-naphthyl methyl) Ether (VI).—1-(Chloromethyl)-4-methyl-2,3-diethylnaphthalene (0.200 g.) was dissolved in 5 ml. of methanol, 2 drops of concentrated hydrochloric acid was added, and the solution refluxed 15 min. The solvent was removed under vacuum, the residue was dissolved in the minimum amount of boiling hexane, and the solution was cooled to give 0.070 g. (45%), m.p. 184–185°. Recrystallization from hexane gave m.p. 187–187.5°.

The same product was obtained by refluxing the chloromethyl compound with 30% sodium carbonate or potassium hydroxide solution overnight. In this way the yield was 78% of VI, m.p. 188–188.4°. The ultraviolet spectrum in ethanol, λ_{max} mμ (log ε), showed absorption at 218 sh (4.80), 230 (5.14), 236 (5.19), 263 sh (3.65), 274 sh (3.91), 284 (4.09), 294 (4.18), 305.5 (4.07), 323 (3.17), and 326 sh (3.07).

Anal. Calcd. for $C_{32}H_{38}O$ (438.6): C, 87.67; H, 8.67. Found: C, 87.22; H, 8.88.

1-Naphthylacetic Acid (VII).—Magnesium turnings (1.26 g.) and 10 ml. of dry ether were added to a nitrogen-filled flask, ethylene bromide (5 drops) and 10% of a solution of 1-(chloromethyl)naphthalene (3 g. in 25 ml. of dry ether) were added. After heating to 30° for 1 hr., no apparent reaction had occurred. Addition of a small crystal of iodine started the reaction and the initial yellow-brown color turned greenish yellow. Thereupon, the remaining 90% of the chloromethylnaphthalene solution was added during 90 min. at 25–30°. After standing overnight under nitrogen, dry carbon dioxide was passed through the solution for 15 min., forming a white precipitate. The ether was removed, the residue was dissolved in methanol, and the solution was clarified with carbon and then evaporated to dryness to leave 0.85 g. (27%) of product, m.p. 121–124°. Solution in dilute alkali, filtration of the alkaline solution, and acidification of the filtrate gave a pure product, m.p. 127–127.5°, lit.[6] m.p. 127°.

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The Structure of the Morpholine β-Iodophenylacetylene Complex

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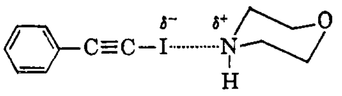
The crystalline compound, $C_{12}H_{14}ONI$, which is formed when morpholine and β-iodophenylacetylene react exothermically has been examined by X-ray crystal structure analysis. The results are in agreement with the charge transfer formula I, which was suggested by Southwick and Kirchner[1] to be the possibility most consistent with the chemical and physical properties of the compound. The alternative possibilities represented by formulas II and III have been shown to be incorrect.



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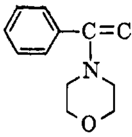
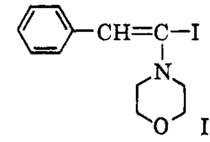


II



III

The complex forms clear, colorless, prismatic crystals which deteriorate and become yellow when exposed to X-rays. The crystal data are as follows: monoclinic, space group $P2_1/c$, uniquely determined from the systematic extinctions ($h0l$) absent for $l = 2n + 1$, ($0k0$) absent for $k = 2n + 1$; cell dimensions $a = 8.97 \pm 0.01$ Å., $b = 4.93 \pm 0.01$ Å., $c = 29.48 \pm 0.04$ Å., $\beta = 96.2 \pm 1.0°$, $V = 1295$ $Å.^3$. With four molecules in the unit cell, the calculated density is 1.75 $g./cm.^2$. Due to the instability of the crystals in a wide range of solvents, a reliable measurements of density could not be made.

The structure was determined from the Fourier projection down the short b axis, using the iodine position for the heavy-atom phase determination of the ($h0l$) structure factors. The iodine coordinates were obtained from the b axis Patterson projection. With the observed structure amplitudes and the calculated structure phases from the iodine contribution alone, the Fourier projection shown in Fig. 1 was obtained. All atoms except the hydrogens were clearly resolved. With only the iodine contribution a structure factor agreement index of 0.24 was obtained. Using the

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