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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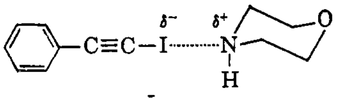
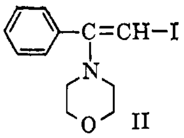
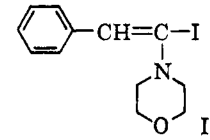
The crystalline compound, $C_{12}H_{14}ONI$, which is formed when morpholine and β-iodophenylacetylene react exothermically has been examined by X-ray crystal structure analysis. The results are in agreement with the charge transfer formula I, which was suggested by Southwick and Kirchner[1] to be the 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.



I



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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(1) P. L. Southwick and J. R. Kirchner, *J. Org. Chem.*, **27**, 3305 (1962).

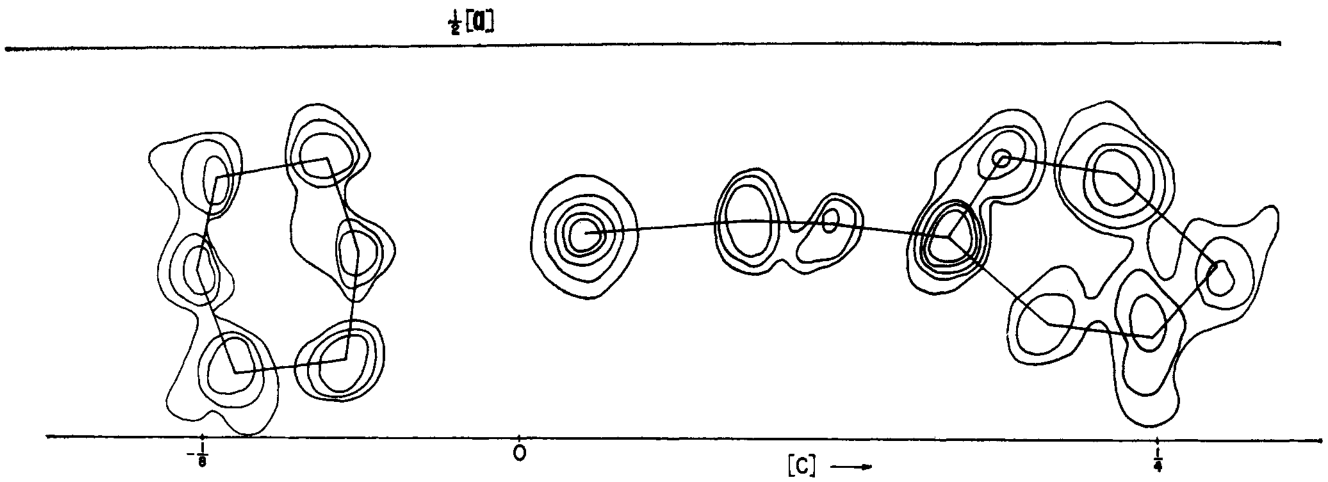

Fig. 1.—Electron density projection of the $C_{12}H_{14}ONI$ complex; contour levels 1/Å.^{2} starting at three, for C, N, O; contour levels 20e/Å.^{2} for I, starting at ten.

atomic coordinates calculated from the Fourier projection, there was one significant phase change and a better agreement factor of $R = 0.18$ was obtained. The slight apparent departure from linearity of the side-chain portion of iodophenylacetylene which is indicated in Fig. 1 may represent experimental error.

Southwick and Kirchner proposed structures I, II, or III for the compound $C_{12}H_{14}ONI$. After considering the results of hydrogenation or reduction with lithium aluminum hydride, and the infrared, ultraviolet, and nuclear magnetic resonance spectra, they concluded that I is most probably the correct structure. However, owing to the instability of the compound, they regarded their structure determination as inconclusive and suggested this X-ray structure determination.

The exclusion of formulas II and III is unambiguous on the basis of the Fourier projection shown in Fig. 1. The only alternatives to formula I which remain would be others of the same geometry as I but having the iodine atom adjacent not to the nitrogen of the morpholine structure, but to a different atom, such as the oxygen.

The existence of other charge transfer complexes in which a basic nitrogen is coordinated with the iodine of an organic iodide[2] suggests that formula I is indeed the correct representation of the substance. Bjornvatten and Hassel[2] found the length of the iodine–nitrogen bond in the quinoline–iodoform complex to be 2.99 Å. The iodine to nitrogen distance in the Fourier *projection*, shown in Fig. 1, is 2.51 Å., which is compatible with an *actual* distance of about 2.9 Å.

An isotropic temperature factor of 2.5 Å.$^{-2}$ was assumed for the iodine and one of 4.0 Å.$^{-2}$ for the light atoms.

Experimental

Owing to the instability of the compound and the frequency of twinning, much difficulty was experienced in obtaining a crystal suitable for X-ray diffraction intensity measurements. A small untwinned crystal, grown by slow evaporation of a normal hexane solution, was sealed in a 0.3-mm. glass capillary. Upon exposure to X-rays for about 80 hr., some decomposition was indicated by a color and shape change of the crystal and by a spread of the diffraction spectra.

The intensity measurements were made visually from CuKα multifilm Weissenberg photographs. For many high angle reflections the CuKα_1 and CuKα_2 spectra were completely resolved. For these reflections the intensity of the CuKα_1 reflection was measured and multipled by a factor of 1.5. For partially resolved reflections a linear interpolation method due to Sakurai[3] was used. After interfilm scaling and averaging of resulting intensity values, the 292 observed ($h0l$) intensities were reduced to structure factor amplitudes by the standard Lorentz and polarization corrections. About 36 reflections were observed to have intensities too small to be measured and these were arbitrarily assigned a value of one-third of the weakest intensity measureable. No absorption corrections were applied to the data. The computations were carried out on an IBM 1620 computer using the programs of Shiono, Hall, and Chu,[4] and of Beurskens.[5]

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(2) T. Bjornvatten and O. Hassel, *Acta Chem. Scand.*, **13**, 1261 (1959).

(3) T. Sakurai, *Acta Cryst.*, **15**, 443 (1962).

(4) R. Shiono, D. Hall, and S. Chu, Technical Report No. 43, The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh, Pa.

(5) P. Beurskens, The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh, Pa., unpublished work.

The Cuprous Chloride-Catalyzed Reaction of Diazomethane with Norbornene Derivatives

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The cuprous ion-catalyzed reaction of diazomethane with olefins recently has been applied in syntheses of cyclopropyl compounds from a number of cyclic hydrocarbons.[1] The intermediate in this catalyzed reaction is also reactive enough to form cyclopropyl derivatives or homologs directly from aromatic compounds.[1,2] We should like to report the stereochemistry of this reaction with regard to formation of cyclopropyl compounds

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(1) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961); J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962).

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