Evaporation of the ether solutions gave a red oil that failed to crystallize and gave a picrate that did not melt below 350°.

The Morpholine-Iodophenylacetylene Adduct or Charge-Transfer Complex. Formation and Conversion to N-Styrylmorpholine[1]

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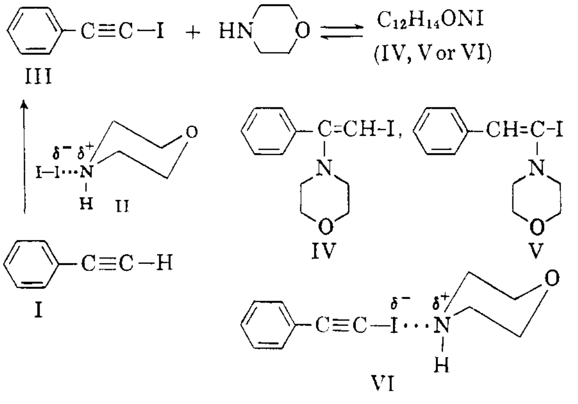
Received August 5, 1961

We have found that morpholine and iodophenylacetylene (III) (1-iodo-2-phenylethyne) react exothermically to form a solid 1:1 adduct. The compound crystallized from petroleum ether in the form of flat, colorless needles or plates, m.p. 75–76° dec. and yielded analytical data agreeing well with the formula $C_{12}H_{14}ONI$. The substance is readily accessible; it can be made directly from phenylacetylene (I) by treating that compound with the iodine-morpholine complex (II)[3,4] and excess morpholine in methanol solution at room temperature. The second method of preparation probably involves intermediate formation of iodophenylacetylene (III). We have made a preliminary investigation of the chemistry of the adduct with the purpose of elucidating its structure. However, the behavior of the compound, although interesting, has been such as to render structure determination by chemical methods somewhat inconclusive.



The most characteristic feature of the behavior of the adduct was its ease of decomposition to morpholine and iodophenylacetylene. It was this property which made it difficult to reach secure conclusions regarding the structure of the substance. When merely suspended in water for several hours at room temperature it dissociated. The morpholine dissolved in the water, leaving iodophenylacetylene as a layer of oil. Catalytic hydrogenation over a Raney nickel catalyst performed in excess morpholine as the solvent resulted in the formation of ethylbenzene. Reduction with lithium aluminum hydride in ether yielded phenylacetylene. It was expected that if the adduct had structure IV or V these reduction procedures would lead to stable products in which the moiety derived from phenylacetylene would be linked to the morpholine nitrogen. The fact that this expectation was not fulfilled may mean that the parts of the adduct are not linked by a carbon-nitrogen bond.

The infrared spectrum of the adduct, determined on a Nujol mull to minimize the possibility of dissociation, resembled that expected for a mixture of morpholine and iodophenylacetylene. There was, for example, a band at 3.06 μ which could be assigned to the N—H bond. It was therefore concluded that the adduct could not correspond to formulas IV or V unless such structures would undergo dissociation even when the compound was merely suspended in Nujol. The ultraviolet spectrum, determined in cyclohexane solution, was virtually identical with that of iodophenylacetylene, a result that may reflect dissociation of the adduct in the dilute solution used for the measurement. There is no reason to suppose either that a compound of structure IV or V would have the same ultraviolet spectrum as iodophenylacetylene or that it would be so unstable as to dissociate almost completely upon being dissolved in cyclohexane.[5]

The nuclear magnetic resonance spectrum (60 Mc.), likewise measured on a cyclohexane solution, was entirely blank in the region between the phenyl pattern at $\tau = 2.50$ to 2.90 p.p.m. and the morpholine A_2B_2 pattern at $\tau = 6.40$ to 7.35 p.p.m.; the one-proton singlet due to vinyl hydrogen expected from structure IV or V was either entirely absent or else hidden by the phenyl pattern. The latter possibility is unlikely; the n.m.r. data provided no support for structure IV or V.

The properties of the morpholine-iodophenylacetylene compound are reminiscent of those reported by Nef[6] for the aniline-iodophenylacetylene

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(1) Based on a portion of a thesis submitted by Jack R. Kirchner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1958.

(2) DuPont Fellow in Chemistry, 1957–1958.

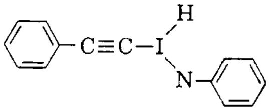
(3) R. V. Rice and G. D. Beal, U. S. Patent, 2,290,710 (July 21, 1943); *Chem. Abstr.*, **37**, 502 (1943).

(4) For other reactions of the iodine-morpholine complex see (a) P. L. Southwick and D. R. Christman, *J. Am. Chem. Soc.*, **74**, 1886 (1952); (b) **75**, 629 (1953). Formula II represents the compound as a charge-transfer complex. It was pointed out previously (ref. 4a) that in some of its reactions the complex may be regarded as equivalent to a hydroiodide of N-iodomorpholine.

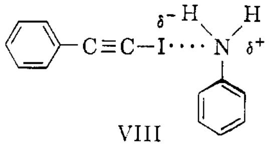
(5) If it could be assumed that in excess morpholine as the solvent the same 1:1 compound would exist, then it could be concluded that the substance probably did dissociate in the cyclohexane solution used for the ultraviolet measurement. The ultraviolet spectrum in morpholine solution shows a maximum at 264 mμ, ε 20,900, whereas the 1:1 compound (or iodophenylacetylene) has its strong absorption at 247 mμ, ε 20,500, in cyclohexane. Solvent absorption obscured any absorption which might have been evident below *ca.* 260 mμ in the determination made in morpholine solution.

(6) J. Nef, *Ann.*, **308**, 293 (1899).

adduct, m.p. 44–46°, which appears to be the only closely related compound previously described. The latter substance yielded iodophenylacetylene plus acetanilide when treated with acetic anhydride, and phenylacetylene plus aniline when treated with zinc dust and ethanol. Iodine in ether converted it to 1,1,2-triiodo-2-phenylethene plus aniline, and thermal decomposition gave phenylacetylene, iodine, and *p*-iodoaniline. Nef felt that these results established the presence of trivalent iodine as in formula VII. Amines are now known to form charge-transfer complexes not only with halogen molecules,[7] X_2, but also with the halogen atoms of at least one organic compound (iodoform) in which the acceptor halogen is subject to the inductive effect of additional halogen atoms.[8] This fact suggests the possibility that both the morpholine-iodophenylacetylene adduct and Nef's compound are nitrogen-to-iodine charge-transfer complexes which may have the structures VI and VIII, respectively.[9] A structure determination performed on the crystalline solids by the X-ray crystallographic method would no doubt be necessary to establish the structures of these substances in an unequivocal manner.

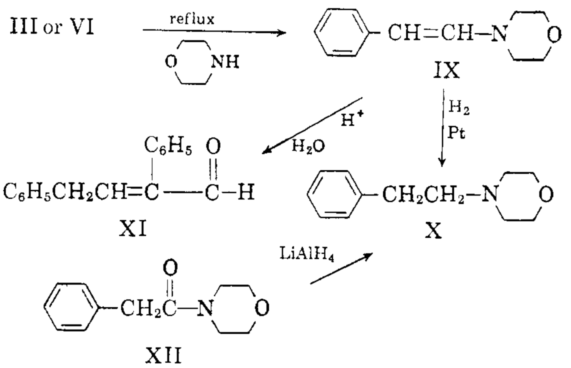


VII



VIII

Iodophenylacetylene did yield a product containing both the morpholine and phenylacetylene moieties when refluxed in excess morpholine; it was converted in quantitative yield to N-styrylmorpholine (IX), m.p. 75-76°.[10] The structure of this crystalline product was evident from the facts that catalytic hydrogenation converted it to N-β-phenylethylmorpholine (X), and acid hydrolysis gave an oil which corresponded in composition and infrared spectrum to the phenylacetaldehyde aldol condensation product, α,γ-diphenylcrotonaldehyde (XI).[11] The oil yielded a 2,4-dinitrophenylhydrazone of the proper composition for the derivative of XI. A comparison sample of X was prepared by lithium aluminum hydride reduction of N-phenylacetylmorpholine (XII); the samples were compared as picrates.



It is possible to envision a number of possible mechanisms which could lead to the formation of N-styrylmorpholine (IX). For example, a charge-transfer complex VI could rearrange to the adduct V, which might then undergo reductive removal of the iodine atom. The formation of N-styrylmorpholine was accompanied by precipitation of a very insoluble hydroiodide, m.p. 306°, which proved not to be morpholine hydroiodide. The constitution of this substance was not established, but its composition suggested that it was the hydroiodide of a base containing two nitrogen atoms and was probably derived from two morpholine molecules. If morpholine hydroiodide were somehow formed in small amounts in the reaction mixture, it might reduce V to N-styrylmorpholine (IX). The iodine so produced might then react with morpholine to yield first the complex II, then N-iodomorpholine plus morpholine hydroiodide. The morpholine hydroiodide could then reduce more of compound V; the N-iodomorpholine might react with morpholine to yield other products, of which the compound melting at 306° may be one. This method of forming N-styrylmorpholine may be related to the conversion of an ethynyl prophyrin derivative into a

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(7) See review by O. Hassel, *Mol. Phys.*, **1**, 241 (1958).

(8) (a) T. Bjornvatten and O. Hassel, *Acta Chem. Scand.*, **13**, 1261 (1959), recently reported that X-ray crystallographic analysis shows that in the 3:1 complex of quinoline with iodoform each iodine is bonded to the nitrogen of a quinoline molecule in a linear N—I—C configuration. Reports have appeared of the formation of other complexes of amines and of dioxane with organic compounds containing two or more halogen atoms which can interact electronically, and nitrogen-halogen or oxygen-halogen bonding in such complexes had been suggested prior to the work of Bjornvatten and Hassel, but had apparently not been demonstrated. See, for example, (b) W. Dehn, *J. Am. Chem. Soc.*, **33**, 1598 (1911); **34**, 290 (1912); (c) W. Dehn and R. Connor, *ibid.*, **34**, 1409 (1912); (d) H. Rheinboldt and A. Luyken, *J. prakt. Chem.*, **133**, 284 (1932); and (e) A. W. Davidson, C. A. VanderWerf, and L. G. Boatright, *J. Am. Chem. Soc.*, **69**, 3045 (1947). Many of the so-called complexes described in the early papers seem actually to have been products of unknown structure formed by irreversible reactions, and a number of true complexes (ref. 8e) exist only at low temperatures.

(9) If the iodophenylacetylene-morpholine compound and Nef's compound are in fact nitrogen-iodine charge-transfer complexes, then it is evident that the phenylethynyl group has functioned as the equivalent of a second halogen atom or a halogenated carbon atom in conferring acceptor properties on the iodine atom. It may be noted that the electron configurations of $\equiv$C—I in iodophenylacetylene bear certain similarities to those of I—I; the four electrons occupying π molecular orbitals on the acetylenic group might be regarded as analogous to the four electrons in π atomic orbitals on an iodine atom in molecular iodine. It has been shown[7] that iodine-amine complexes possess a linear configuration of the atoms I—I—N, and Hassel[7] has suggested that the acceptor iodine in such complexes utilizes $sp^3d_{z^2}$ hybrid orbitals. The complexes VI or VIII might correspond to these iodine-amine complexes both in linear geometry and in electronic configuration.

(10) After our work had been done, W. Ziegenbein and W. Franks, *Chem. Ber.*, **90**, 2291 (1957), reported the preparation of this compound from phenylacetaldehyde and morpholine.

(11) Less than one gram of this substance was obtained and a thorough fractional distillation was not performed. Fully purified material is reported to crystallize to a solid, m.p. 39.5–40°. See J. L. E. Erickson and G. N. Grammer, *J. Am. Chem. Soc.*, **80**, 5469 (1958), and W. Triebs and K. Krumbholz, *Chem. Ber.*, **85**, 1116 (1952). The major infrared bands at 5.91, 6.11, and 6.23 μ in the oil agreed very well with the report by Erickson and Grammer that the pure solid compound has strong absorptions at 5.91, 6.11, and 6.24 μ.

corresponding β-morpholinovinyl prophyrin which Woodward[12] has recently accomplished by heating the ethynyl compound with morpholine and sulfur.

Iodine plus excess morpholine is an effective reagent for the iodination of monosubstituted acetylenes. It was successfully applied to iodination of 1-ethylcyclohexanol, as well as to iodination of phenylacetylene.

Experimental[13]

Reaction of Iodophenylacetylene with Morpholine.—When 1.15 g. (0.0132 mole) of morpholine was added to 3.0 g. (0.0132 mole) of iodophenylacetylene, an off-white solid mass was formed with the evolution of heat. The solid on crystallization from petroleum ether (b.p. 65–110°) yielded 3.247 g. (78.4%) of the morpholine-iodophenylacetylene adduct as colorless needles, m.p. 75–76° dec.

Anal. Calcd. for $C_{12}H_{14}ONI$: C, 45.71; H, 4.44; N, 4.44. Found: C, 45.33; H, 4.35; N, 4.35.

Infrared spectrum[14a] (Nujol mull): 3.06 m, 3.42 s, 3.50 s, 6.24 w, 6.34 w, 6.71 m, 6.84 m, 6.93 m, 7.26 w, 7.33 w. Infrared spectrum (carbon tetrachloride solution): 3.00 w, 3.28 m, 3.44 s, 3.55 s, 3.66 m, 3.75 w, 3.82 w, 4.62 w, 5.09 w, 5.15 w, 5.28 w, 5.32 w, 5.48 w, 5.54 w, 5.66 w, 6.00 w, 6.25 m, 6.36 w, 6.72 s, 6.90 s, 6.94 w. 7.19 w, 7.28 w, 7.43 m. Infrared spectrum[14b] (potassium bromide pellet): 2.93 w (broad), 3.09 m (sharp), 3.41 m, 3.45 m, 3.55 m, 3.70 w, 5.09 w, 5.14 w, 5.24 w, 5.34 w, 5.57 w, 5.74 w. 5.99 w, 6.11 w, 6.26 s, 6.30 w, 6.37 m, 6.44 w, 6.74 s, 6.86 m, 6.93 s, 7.01 m, 7.26 m, 7.39 s, 7.44 w, 7.68 w, 7.77 m, 7.89 w, 8.06 s, 8.27 s, 8.38 m. 8.54 m, 8.70 m. 8.95 m. 9.15 s, 9.38 m, 9.70 s, 9.92 m, 10.12 w, 10.38 w, 10.68 m, 10.98 m, 11.32 s, 11.75 s. 12.12 s, 12.32 m, 12.50 m, 13.18 s, 14.51 s. Since a band due to $C{\equiv}C$ stretching is often of low intensity or absent, the lack of 4.62-μ band in the mull and potassium bromide pellet spectra is of uncertain significance.

The ultraviolet spectrum, determined in cyclohexane solution with a Cary recording spectrophotometer, showed two maxima, λ 247 mμ, ϵ 21,370 and λ 257.5 mν, ϵ 16,170 and two minima, λ 219.5 mμ, ϵ 4540 and λ 255 mμ, ϵ 15,680.

Preparation of the Morpholine-Iodophenylacetylene Adduct from Phenylacetylene and the Morpholine-Iodine Complex.—To the morpholine-iodine complex[3,4] formed with excess morpholine from 21 g. (0.0828 mole) of iodine and 30.0 g. (0.345 mole) of morpholine in 100 ml. of methanol was added 8.46 g. (0.0828 mole) of phenylacetylene. The resultant mixture was allowed to stand at room temperature in an open beaker for several days. Although the red-orange precipitate of the morpholine-iodine complex quickly disappeared in the space of a few hours, the characteristic deep red coloration of the complex in solution faded only slowly on standing. Evaporation of the methanol left a mass of yellow-orange crystals. Extraction with hot petroleum ether (b.p. 65–110°) or *n*-hexane removed the morpholine-iodophenylacetylene compound from the associated morpholine hydroiodide. Cooling of the extract caused crystallization of the morpholine-iodophenylacetylene adduct as long, colorless needles, m.p. 75–76° dec. Average yields of 75% were obtained over a series of runs.

Conversion of the Morpholine-Iodophenylacetylene Adduct to Iodophenylacetylene.—A mixture of 10.0 g. (0.0317 mole) of the adduct and 100 ml. of water was allowed to stand overnight at room temperature. During this period the crystalline material was slowly converted into a heavy, colorless oil. The mixture was extracted with ether. The ether extract was washed successively with 6 *N* hydrochloric acid and water, and dried over anhydrous sodium sulfate. After the drying agent had been removed by filtration and the filtrate concentrated, the residual oil was distilled at 71–74° (*ca.* 1 mm.) to obtain 5.16 g. (71.3%) of iodophenylacetylene as a colorless oil.

The infrared spectrum of the compound was identical with that of an authentic sample of iodophenylacetylene prepared from phenylacetylene by the method of Nef.[6]

Catalytic Reduction of the Morpholine-Iodophenylacetylene Adduct.—A solution of 8.0 g. (0.254 mole) of the morpholine-iodophenylacetylene adduct in 50 ml. of morpholine with *ca.* 100 mg. of Raney nickel W-5 catalyst was reduced in a Parr apparatus for 2.5 hr. Celite was added to the solution and the mixture filtered. The filtrate was diluted with water, acidified with 6 *N* hydrochloric acid, and extracted with ether. The ether extract was concentrated by evaporation to obtain 2.7 g. (100%) of ethylbenzene as a light yellow oil. The product distilled as a colorless oil, b.p. 134°; the infrared spectrum was identical with that of an authentic sample of ethylbenzene.

Treatment of Morpholine-Iodophenylacetylene Adduct with Lithium Aluminum Hydride.—An ethereal solution of 10 g. (0.0317 mole) of the morpholine-iodophenylacetylene adduct was added to an ether slurry of lithium aluminum hydride. The mixture was stirred at room temperature for 2 hr. After the excess hydride had been decomposed by the addition of a saturated aqueous solution of sodium potassium tartrate, the ether fraction was removed and concentrated by evaporation. There was obtained 2.5 g. (78.1%) of phenylacetylene as a light yellow oil. A solution of the oil and iodine in methanol was allowed to stand at room temperature while the solvent evaporated. The residual solid was crystallized from 95% ethanol to obtain α,β-diiodostyrene as small, colorless crystals, m.p. 75–76°. The compound did not depress the melting point of an authentic sample of α,β-diiodostyrene prepared from phenylacetylene by the method of Peratoner,[15] and the infrared spectra of the two samples were identical.

Preparation of N-Styrylmorpholine from the Morpholine-Iodophenylacetylene Adduct and Morpholine.—A solution of 10.6 g. (0.0336 mole) of the morpholine-iodophenylacetylene adduct in 100 ml. of morpholine was heated under reflux for 48 hr. The clear solution clouded with a suspension of fine particles after *ca.* 15 min. of refluxing; a clear, deep red solution formed on continued heating. The solution was cooled, diluted with ammonium hydroxide, and refrigerated overnight. The orange solid which precipitated was removed by filtration and dried to obtain 6.4 g. (100%) of crude N-styrylmorpholine. The compound crystallized from petroleum ether (b.p. 30–60°) as light orange platelets, m.p. 75–76° dec.[16]

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.19; H, 7.94; N, 7.40. Found: C, 76.16; H, 7.94; N, 7.35.

Infrared spectrum[14a] (carbon disulfide solution): 3.26 m, 3.29 m, 3.37 m, 3.44 m, 3.50 s, 3.52 s, 6.09 s, 7.26 s, 7.42 s, 7.50 m.

The suspension of fine particles that appears early in the reflux period was investigated in several runs. In one run the reaction mixture was poured into aqueous ammonium hydroxide after it became turbid. The insoluble, light tan

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[12] Described by Professor R. B. Woodward in the Roger Adams Medal Award Address before the Seventeenth National Organic Chemistry Symposium, Bloomington, Indiana, June 27, 1961.

[13] Microanalyses by Drs. G. Weiler and F. B. Strauss, Oxford, England, and Geller Laboratories, Bardonia, New York.

[14] (a) The infrared spectra of Nujol mulls and carbon tetrachloride or carbon disulfide solutions were measured with a Perkin-Elmer Model 21 spectrophotometer. Absorption bands (wave length in μ) are given over the range 2.5 to 7.5 μ; (b) A potassium bromide pellet spectrum, measured with a Baird Model B spectrophotometer, is described for the range 2 to 15 μ. The letters s, m, and w designate strong, medium, and weak bands, respectively.

[15] A. Peratoner, *Gazz. chim ital.*, **22**, II, 69 (1892).

[16] The light orange tint of the crystals probably indicates a trace of a decomposition product; Ziegenbein and Franks, ref. 10, described the substance as colorless crystals, m.p. 77–78°, which became colored and developed an odor of phenylacetaldehyde when allowed to stand in the air.

particles were removed by filtration and dried; m.p. 306° dec.

Anal. Calcd. for $C_8H_{15}IN_2O$: C, 34.06; H, 5.39; N, 9.94. Found: C, 35.84; H, 5.50; N, 9.06.

When the reaction mixture in another run was filtered after becoming turbid, a tan solid, melting at 295° dec., was obtained. The compound crystallized from 47% hydroiodic acid as yellow crystals, m.p. 297° dec. The melting point appeared to vary with the rate of heating.

Anal. Found: C, 35.05; H, 5.18; N, 9.60.

Conversion of N-Styrylmorpholine to N-β-Phenylethylmorpholine.—A sample of N-styrylmorpholine in methanol was reduced using Adams' platinum oxide catalyst in a Parr apparatus. The N-β-phenylethylmorpholine which was obtained as an oil after catalyst and solvent had been removed was converted to a picrate by treatment with ethanolic picric acid. The compound crystallized from 95% ethanol as yellow needles, m.p. 165–166°.

Anal. Calcd. for $C_{18}H_{29}N_4O_8$: C, 51.43; H, 4.76; N, 13.33. Found: C, 51.16; H, 4.81; N, 12.80.

The compound did not depress the melting point of an authentic sample of N-β-phenylethylmorpholine picrate prepared by the following sequence of reactions: N-phenylacetylmorpholine prepared from phenylacetyl chloride and morpholine was reduced with lithium aluminum hydride. The N-β-phenylethylmorpholine obtained as a light brown oil was converted to the picrate with ethanolic picric acid. The picrate crystallized from 95% ethanol as yellow needles, m.p. 165–166°.

Conversion of *N*-Styrylmorpholine to α,γ-Diphenylcrotonaldehyde.—To 2.0 g. (0.0105 mole) of N-styrylmorpholine was added dropwise with stirring 10 ml. of 98–100% formic acid.[17] The mixture was cooled in an ice bath during the addition and until all solid had dissolved. The clear orange solution was warmed on a steam bath for 30 min., cooled, diluted with 10 ml. of 3 *N* hydrochloric acid, and extracted with 50 ml. of ether. The ether extract was re-extracted with 10 ml. of 3 *N* hydrochloric acid and concentrated to obtain a brown oil. The oil was distilled to obtain 663 mg. (56.8%) of α,γ-diphenylcrotonaldehyde as a light yellow oil, b.p. 152° (*ca.* 2 mm.).[11]

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.28; H, 6.45.

The oil yielded an orange 2,4-dinitrophenylhydrazone, m.p. 194–195° after crystallization from 95% ethanol.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.63; H, 4.86; N, 13.8.

The compound did not depress the melting point of the 2,4-dinitrophenylhydrazone obtained from a sample of α,γ-diphenylcrotonaldehyde prepared by the method of Lindermann.[18]

Preparation of 1-(Iodoethynyl)cyclohexanol.—To the morpholine-iodine complex formed from 28 g. (0.11 mole) of iodine and 40 g. (0.46 mole) of morpholine in 200 ml. of methanol was added 13.6 g. (0.11 mole) of 1-ethynylcyclohexanol. After the mixture had stood at room temperature for 2 days, it was evaporated to half its volume and diluted with ether. The solid which precipitated was removed by filtration, washed with ether, and dried to obtain morpholine hydroiodide as light yellow needles, m.p. 212–213° dec. The filtrate was concentrated by evaporation to obtain a thick red oil. The oil was triturated in water and the mixture allowed to stand at room temperature while the oil solidified. The solid was removed by filtration and dried to obtain 25 g. (91.2%) of crude 1-(iodoethynyl)cyclohexanol. The product crystallized from petroleum ether (b.p. 65–110°) as colorless needles, m.p. 88–89°.

Anal. Calcd. for $C_8H_{11}IO$: C, 38.42; H, 4.43. Found: C, 38.69; H, 4.35.

Acknowledgment.—The authors are indebted to Dr. Frank O. Ellison for advice concerning the valence structure of the charge-transfer complex, to Dr. Robert J. Kurland for the n.m.r. determination, and to Dr. Norbert M. Zaczek for ultraviolet measurements.

2-Fluorocyclohexanol

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December 4, 1961

Although 2-fluorocyclohexyl acetate has been prepared[2] by acetylation of 2-chlorocyclohexanol and subsequent treatment with potassium fluoride, the literature reveals no record of the parent substance, 2-fluorocyclohexanol. Several unsuccessful attempts were made in this laboratory to prepare the fluoro alcohol. One such experiment involved treatment of 2-chlorocyclohexanol with potassium fluoride as described by Knunyants and co-workers[3] for ethylene chlorohydrin. It was also shown[4] that the action of anhydrous hydrogen fluoride under various conditions resulted in chain polymerization of ethylene oxide to yield polyethylene glycols and polyethylene fluorohydrins. However, in their attempts to minimize polymerization by adding a large amount of ethyl ether as a solvent, they obtained ethylene fluorohydrin in 40% yield.

Various epoxides in the steroid series have been converted to the corresponding fluorohydrins in good yields by treatment with anhydrous hydrogen fluoride in tetrahydrofuran and chloroform.[5,6]

According to some of these workers tetrahydrofuran behaves as a base, increasing the effective concentration of fluoride ion without inhibiting completely the acid catalysis necessary for epoxide ring opening. It therefore seemed quite possible that sodium bifluoride would behave in a similar manner and that heating an epoxide such as cyclohexene oxide, with this reagent being a controlled source of anhydrous hydrogen fluoride, the corresponding fluorohydrin would be produced. The

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[17] The reaction conditions were those recommended by P. de Benneville and J. Macartney, *J. Am. Chem. Soc.*, **72**, 3073 (1950) for reduction of enamines. In this case little reduction apparently occurred, and hydrolysis followed by aldol condensation was promoted.

[18] H. Lindemann, German Patent 554,785 (January 13, 1931); *Chem. Abstr.*, **26**, 6080 (1932).

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[2] E. Gryszkiewicz-Trochimow, A. Sporzynski, and J. Wnuk, *Rec. trav. chim.*, **66**, 413 (1947).

[3] I. L. Knunyants, O. V. Kil'dasheva, and E. Bukovskaya, *J. Gen. Chem. USSR*, **19**, 93 (1949).

[4] I. L. Knunyants, O. V. Kil'dasheva, and I. P. Petrov, *ibid.*, **19**, 87 (1949).

[5] R. F. Hirschmann, R. Miller, J. Wood, and R. E. Jones, *J. Am. Chem. Soc.*, **78**, 4956 (1956).

[6] D. Taub, R. D. Hoffsommer, and N. L. Wendler, *ibid.*, **79**, 452 (1957).