usual manner in boiling alcohol gave the corresponding acrolein derivative.

The semicarbazone could not be isolated.

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Di-(*p*-halophenyl)-methylcarbinols

BY OLIVER GRUMMITT, DEAN MARSH AND JAMES A. STEARNS

The miticidal activity of di-(*p*-chlorophenyl)-methylcarbinol[1,2] led to the synthesis of the analogous fluoro-, bromo- and iodocompounds. In each case the carbinol was made in good yield by the action of methylmagnesium bromide on the *p,p'*-dihalobenzophenone.[2]

The ultraviolet absorption spectra of these four carbinols, along with the unsubstituted diphenylmethylcarbinol, shown in Fig. 1, are of particular interest because of differences due to the halogen atoms. The chlorine, bromine and iodine compounds show pronounced maxima in the range of 225–240 mμ with a shift to the longer wave length for the iodine derivative. The iodine substituted carbinol is most strongly absorbent and its maximum is at the longest wave length, 240 mμ. The bromine and chlorine derivatives are both less absorbent, the former is slightly stronger, but the location of the peaks at 225–227 mμ is virtually identical. On the other hand, the fluoro- and the unsubstituted carbinols show no absorption peaks throughout the range observed (215–270 mμ).

Experimental

Diphenylmethylcarbinol.—A sample melting 78–80° was made from phenylmagnesium bromide and ethyl acetate.[3]

Di-(*p*-chlorophenyl)-methylcarbinol.—A sample melting 69–69.5° was made from *p,p'*-dichlorobenzophenone and methylmagnesium bromide.[2]

Di-(*p*-fluorophenyl)-methylcarbinol.—The general procedure for this preparation and for the bromo- and iodocarbinols paralleled the preparation of the chlorocarbinol.[2] From 5 g. (0.023 mole) of *p,p'*-difluorobenzophenone (m. p. 105.5–107°) and 11.5 ml. of 2.2 *N* methylmagnesium bromide (0.025 mole) there was obtained 4.3 g., 80%, of carbinol as a light yellow oil which did not crystallize at 0°; $n^{25}{}_D$ 1.5502.

Anal.[4] Calcd. for $C_{14}H_{12}OF_2$: C, 71.8; H, 5.17; F, 16.2. Found: C, 73.2; H, 5.20; F, 16.5.

p,p'-Difluorobenzophenone was obtained by the Friedel–Crafts reaction of fluorobenzene and carbon tetrachloride in 43% yield, m. p. 102–105°.[5]

Di-(*p*-bromophenyl)-methylcarbinol.—From 40.0 g. (0.089 mole) of *p,p'*-dibromobenzophenone (m. p. 173.5–175°) and 43 ml. of 2.2 *N* methylmagnesium bromide (0.095 mole) there was obtained 36.1 g. (88.7%) of crude carbinol melting 81.5–84°. Crystallization of 5 g. from petroleum ether (b. p. 60–70°) gave 3.2 g. melting 83.5–85.5°.

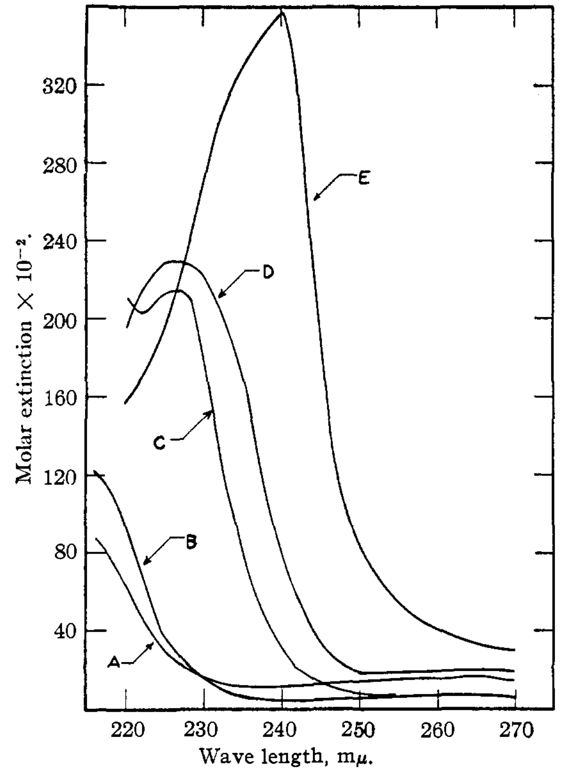

Fig. 1.—The ultraviolet absorption spectra of (A) di-(*p*-fluorophenyl)-methylcarbinol, (B) diphenylmethylcarbinol, (C) di-(*p*-chlorophenyl)-methylcarbinol, (D) di-(*p*-bromophenyl)-methylcarbinol, and (E) di-(*p*-iodophenyl)-methylcarbinol.

Anal. Calcd. for $C_{14}H_{12}OBr_2$: Br, 44.9. Found: Br, 45.2.

The *p,p'*-dibromobenzophenone was made in 23.4% yield by the Friedel–Crafts reaction of bromobenzene and carbon tetrachloride.[6]

The melting point of the carbinol, 83.5–85.5°, was almost identical with that of the 1,1-di-(*p*-bromophenyl)-ethylene, 84°, made by vacuum distillation of the carbinol.[7] To make certain that these were two different compounds a 5-g. portion of the carbinol was dehydrated by heating at 210° for twenty minutes, then refluxed with 5 ml. of 20% sulfuric acid for one-half hour. Crystallization of the crude ethylene from methanol gave 2.4 g. melting 84–85°. A mixed melting point of this ethylene with the carbinol was 57–69°.

Di-(*p*-iodophenyl)-methylcarbinol.—From 0.7 g. (0.0016 mole) of *p,p'*-diiodobenzophenone (m. p. 234–237°) and 5 ml. of 2 *N* methylmagnesium bromide (0.05 mole) there was obtained 0.5 g., 69.0%, of carbinol melting 108–109°. Two more crystallizations raised the melting point to 110–111°.

Anal. Calcd. for $C_{14}H_{12}OI_2$: I, 56.4. Found: I, 55.8.

This compound is not stable at room temperature. After a few weeks in a closed tube it turns yellow, there is an odor of iodine or possibly hydrogen iodide, and the iodine content found by analysis is lower than the calculated value.

p,p'-Diiodobenzophenone is a difficult ketone to obtain by the usual Friedel–Crafts routes. Iodobenzene with

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[1] U. S. Patent 2,430,586, November 11, 1947, R. F. Ruthruff, Oliver Grummitt and B. C. Dickinson.

[2] Grummitt, Buck and Becker, THIS JOURNAL, **67**, 2265 (1945).

[3] "Org. Syntheses," Coll. Vol. I, p. 226 (1941).

[4] By the Clark Microanalytical Laboratory, Urbana, Illinois.

[5] Bergmann, Hoffman and Meyer, *J. prakt. Chem.*, **135**, 245 (1932).

[6] Norris and Green, *Am. Chem. J.*, **26**, 497 (1901).

[7] Ashley, Grove and Henshall, *J. Chem. Soc.*, 261 (1948).

carbon tetrachloride under conditions suitable for benzophenone,[8] *p,p'*-difluorobenzophenone[6] and *p,p'*-dibromobenzophenone[6] liberated much free iodine and yielded no ketone. *p*-Iodobenzoyl chloride (from *p*-iodobenzoic acid[9] and phosphorus pentachloride) and iodobenzene gave only a 1.6% of ketone.[10]

Ultraviolet Spectra.—The measurements were made with a model DU Beckman ultraviolet spectrophotometer using 1 cm. square quartz cells and spectroscopically pure isooctane as the solvent.

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(8) "Org. Syntheses," Coll. Vol. I, p. 95 (1941).

(9) "Org. Syntheses," Coll. Vol. I, p. 325 (1941).

(10) Montagne, *Ber.*, **51**, 1486 (1918).

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N-Chloromorpholine and Related Compounds[1]

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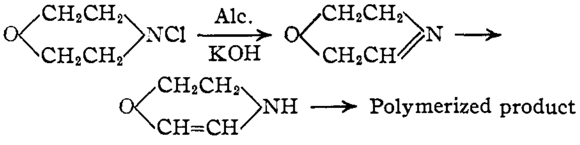
Morpholine reacts with aqueous solutions of sodium hypohalites to give the corresponding N-halogen substituted compounds.[3] Both N-chloro- and N-bromomorpholine rapidly undergo intermolecular dehydrohalogenation on standing to yield morpholine hydrohalide and polymerized dehydromorpholine derivatives. The dehydrohalogenation of N-chloromorpholine with alcoholic potassium hydroxide yields high-boiling, polymerized forms of dehydromorpholine rather than a monomer. This is in agreement with work done on the dehydrohalogenation of N-chloropiperidine.[4] A rearrangement of the double bond occurs in this process since the resulting compounds still show reactions of the imino group.



N-Chloromorpholine reacts slowly with phenyl or α-naphthyl isocyanate to form chloro-substituted ureas. A mechanism involving the addition of the chloromorpholine to the double bond system of the isocyanate, followed by a rearrangement of the intermediate N-chlorourea in the same manner as N-chloroacetanilide, accounts for the products. Identical products are obtained by the action of sodium hypochlorite on the corresponding unsubstituted ureas. N-Cyano- and N-hydroxymorpholine also have been prepared.

Experimental

N-Chloromorpholine.—A quantitative yield of the chloromorpholine was obtained when 39 g. of morpholine (0.45 mole) in 50 ml. of water was added slowly with stirring to 300 ml. of 1.5 molar sodium hypochlorite (0.45 mole), maintained at 0°; pale yellow or colorless oil, b. p. 52–53° at 17 mm. Vigorous decomposition occurs if the distillation is performed at atmospheric pressure.

N-Chloromorpholine possesses a very acrid odor, has lachrymatory properties, and produces a burning sensation when applied to the skin. It does not cause the immediate evolution of nitrogen from aqueous solutions of urea although it rapidly liberates iodine from potassium iodide solution. The freshly distilled product darkens rapidly and begins to deposit crystals of morpholine hydrochloride within six to eight hours. Ten grams of N-chloromorpholine allowed to stand for three months in a sealed tube changed to a dark brown solid. All of this solid dissolved in cold water, except 0.5 g. of an amorphous residue, softening at 95–100° and decomposing at about 120°. The water soluble fraction was evaporated to dryness and treated with 50% solution of sodium hydroxide. The separated oil was taken up in ether, dried over anhydrous potassium carbonate, and distilled. Only morpholine was identified (as its naphthyl isocyanate derivative). The dark brown, viscous material remaining in the distilling flask had the characteristics of polymerized dehydromorpholine.

Reaction of N-Chloromorpholine with Amines. (A) With Aniline.—A mixture of 2.4 g. of N-chloromorpholine and 1.9 g. of aniline was allowed to stand for two weeks, after which it was repeatedly extracted with ether, leaving 1.8 g. of morpholine hydrochloride. On steam distilling the acidified extract, 0.3 g. of azobenzene, m. p. 64–65°, was recovered. A mixed melting point with an authentic specimen showed no depression.

(B) With *p*-Toluidine.—From 0.02 molar quantities of the reactants (in benzene to moderate the initial vigorous reaction) was recovered 0.3 g. of 4,4'-azotoluene.[5]

(C) With Morpholine.—Only a small amount of a yellow oil, b. p. 116–118° at 28 mm., was isolated from the reaction of morpholine with N-chloromorpholine. Since the product reacted with α-naphthyl isocyanate, indicating the presence of imino groups, it was probably dehydromorpholine and not N,N'-dimorpholine.

Dehydrohalogenation of N-Chloromorpholine.—N-Chloromorpholine (31.6 g.) was added dropwise with shaking to 180 g. of a refluxing, 10% alcoholic potash solution. After heating for an additional thirty minutes, the alcohol was evaporated and the residue dissolved in a minimum of water. This aqueous solution was then continuously extracted with ether until the extractant was colorless; after desiccating the ethereal solution with anhydrous potassium carbonate, the ether was removed. Distillation of the residual oil gave no plateaus in the distillation curve between 40 and 170° at 26 mm. Material boiling below 40° at 26 mm. was morpholine; above 170° the residue in the still-pot charred. A middle cut, b. p. 75–120°, was a yellow viscous oil which slowly crystallized to white masses, m. p. 105–106°.[6]

Anal. Calcd. for $(C_4H_7ON)_x$: N, 16.48. Found: N, 16.22.

This material was readily soluble in water, acids, and alcohol; difficultly soluble in ether. The α-naphthyl isocyanate derivative crystallized from a mixture of ethyl ether and petroleum ether as a white amorphous powder, m. p. 175–180°, after forming a sticky foam at 134–135°. The acetyl derivative boiled at 230–232° at 760 mm.

Anal. Calcd. for $C_6H_{11}O_2N$: N, 10.83. Found: N, 10.73.

Reaction of N-Chloromorpholine with Isocyanates. (A) With Phenyl Isocyanate.—A solution of 1.2 g. of phenyl isocyanate and 2.4 g. of N-chloromorpholine in 10 ml. of absolute ethyl ether was allowed to stand three days. The solid that separated was removed by filtration and washed with ether to remove excess reactants; yield 1.0 g. One recrystallization from alcohol gave needles melting at 196°.

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(1) From the thesis submitted by R. A. Henry to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, December, 1942.

(2) Present address: Inorganic Chemistry Branch, U. S. Naval Ordnance Test Station, China Lake, Calif.

(3) N-Chloromorpholine has been previously prepared in 54% yield by Myers and Wright, *Can. J. Research*, **26B**, 2681 (1948), by the action of sodium hypochlorite on an acid solution of morpholine.

(4) Lellmann, *Ber.*, **22**, 1319 (1889).

(5) Pierson and Heumann, *Ber.*, **16**, 1048 (1883), prepared 4,4'-azotoluene by treating *p*-toluidine with ethyldichloramine.

(6) The melting points are corrected.