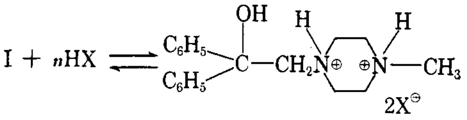
It appears from this study that ionic structure does exert a strong and helpful influence on the hydrogenation of the title compound. Furthermore, we would like to suggest that the difficulty in reducing both rings when starting with the dihydrochloride salt of I can be due to the fact that the conversion of I to Ia is reversible. Therefore, complete or sufficient conversion of the poisoning nitrogen atom, particularly at N^1, to a nonpoisoning form cannot be achieved.



Ia

n = 2 or more; X = Cl, CH_3COO

In the case of the quaternary salt III, a single species, incapable of reversibility, exists at N^1, and only a small amount of acid is necessary to counteract the effect of the other nitrogen atom.

Experimental

Compound II was prepared from I by the method described in the literature[3,4] (experiment I in the Table). Compound IV was prepared from III and identified by melting point and mixture melting point with a known standard.[3,4]

Attempts to Reduce Both Rings.—Experiment I was followed using a 5% weight ratio of platinum oxide. After 48 hr., uptake of hydrogen, which had stopped, amounted to about 4 molar equivalents (3 equivalents were absorbed in 7 hr.). About 70% of impure II dihydrochloride hemihydrate was recovered, plus 25% of a product, which from analysis could be a mixture of the hemihydrate and the anhydrous salt of II, melting up to 255°.[3]

Other attempts with more catalyst or with the base I in glacial acetic acid also failed to go to completion.

1,1-Dimethyl-4-(2,2-dicyclohexyl-2-hydroxyethyl)piperazinium Methosulfate (V).—A solution of 12.67 g. (0.03 mole) of III in 30 ml. of water and 3 ml. (0.05 mole) of glacial acetic acid was hydrogenated under 2-atm. pressure at 55–60° in the presence of 0.63 g. of platinum oxide. Uptake for 0.18 mole (6 H_2) was complete in 20 hr. The solution was filtered from the catalyst and concentrated to dryness under reduced pressure. The residue was treated with anhydrous alcohol and benzene and reconcentrated to ensure complete removal of water and acetic acid. The residue was recrystallized from hot isopropyl alcohol and dried to constant weight before analysis; yield 78%.

Anal. Calcd. for $C_{21}H_{42}N_2O_5S$: C, 58.03; H, 9.74; N, 6.45; O, 18.41; S, 7.38. Found: C, 58.30; H, 9.75; N, 6.58; O, 18.38; S, 7.45.

The melting point of the product varied because of the difficulty of removing water or solvent. After recrystallization, it melted at 175–178°. After thorough drying for 3 days at 100°, the melting point rose to 182–185°.

In a similar reduction 8 g. of 5% rhodium on carbon[5] was used. In another reduction in the absence of acid, 10 g. of the same catalyst brought about uptake of 0.18 moles of hydrogen in 36 hr. (3 equivalents were absorbed in 3 hr.). In each case, V was obtained in 75–80% yield.

Infrared examination of the products of the three experiments showed no evidence of benzenoid structure.

Acknowledgment.—The author is indebted to Mr. E. F. Shelberg (now retired) and Mr. O. Kolsto of this laboratory for the microanalyses and to Mr. W. Washburn also of this laboratory for infrared spectroscopy.

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[3] H. E. Zaugg, R. J. Michaels, H. J. Glenn, L. R. Swett, M. Freifelder, G. R. Stone, and A. W. Weston, *J. Am. Chem. Soc.*, **80**, 2763 (1958).

[4] H. E. Zaugg, M. Freifelder, R. J. Michaels, and A. W. Weston, U. S. Patent 2,980,683 (April 18, 1961).

[5] The rhodium catalysts are available from Engelhard Industries, Newark, N. J.

Condensation of Formaldehyde with Reissert Compounds

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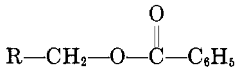
Received August 16, 1963

Formaldehyde has been condensed with Reissert compounds, 2-benzoyl-1,2-dihydroisoquinaldonitrile and 1-benzoyl-1,2-dihydroquinaldonitrile, in a reaction analogous to that previously described for other aldehydes[2–5] to yield 1-isoquinolylcarbinyl benzoate (I) and 2-quinolylcarbinyl benzoate (II), respectively.



$$R{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_6H_5$$

I, R = 1-isoquinolyl
II, R = 2-quinolyl

$R{-}CH_2OH$

III, R = 1-isoquinolyl
IV, R = 2-quinolyl

Saponification of the hydrochlorides of esters I and II gave the expected 1-isoquinolylcarbinol (III) and 2-quinolylcarbinol (IV), respectively. The 1-isoquinolylcarbinol obtained had a melting point of 77–79° as compared with a reported value of 65°.[6] That this was actually 1-isoquinolylcarbinol (III) was confirmed by elementary analysis and by reduction by the method of Buck, *et al.*,[7] to the known 1-methylisoquinoline. This appears to be a more advantageous method for preparing III than that previously described.[6]

Experimental[8]

Hydrochloride of 1-Isoquinolylcarbinyl Benzoate (I).—To a solution of 10.4 g. (0.04 mole) of 2-benzoyl-1,2-dihydroisoquinaldonitrile[9] in 150 ml. of dry ether and 75 ml. of dry dioxane maintained at 0° in an atmosphere of pure nitrogen was added 0.04 mole of freshly prepared phenyllithium. Gaseous formaldehyde, formed by the depolymerization of paraformaldehyde, was introduced into the resultant red solution by means of a slow stream of nitrogen. The addition was continued until the red color was discharged and a white suspension formed. The mixture was stirred for 1 hr. at 0°, then for an additional hour at room temperature. Sufficient ether was added to increase the total volume to 500 ml., and the mixture was extracted with 12 ml. of water and then two 50-ml. portions of 10% hydrochloric acid. Cooling of the hydrochloric acid solution in an ice bath gave a white solid which was removed by filtration. This afforded 7.24 g. (61.4%) of the hydrochloride of I. After several recrystallizations from ethanol, the melting point was 177–180° dec.

Anal. Calcd. for $C_{17}H_{14}ClNO_2$: C, 68.15; H, 4.79; N, 4.67; Cl, 11.83. Found: C, 68.13; H, 4.64; N, 4.82; Cl, 12.07.

1-Isoquinolylcarbinol (III).—This compound was obtained by refluxing a solution of 8.6 g. (0.028 mole) of the hydrochloride of I and 10.0 g. of potassium hydroxide in a mixture of 60 ml. of ethanol and 25 ml. of water for 8 hr. The majority of the ethanol

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[1] Undergraduate Petroleum Research Fund Scholars for academic years, 1961–1962 and 1962–1963, respectively.

[2] L. R. Walters, N. T. Iyer, and W. E. McEwen, *J. Am. Chem. Soc.*, **80**, 1177 (1958).

[3] F. D. Popp and W. E. McEwen, *ibid.*, **79**, 3773 (1957).

[4] F. D. Popp and W. E. McEwen, *ibid.*, **80**, 1181 (1958).

[5] E. G. Podrebarac and W. E. McEwen, *J. Org. Chem.*, **26**, 1165 (1961).

[6] B. R. Brown, D. Ll. Hammick, and B. H. Thewlis, *J. Chem. Soc.*, 1145 (1951).

[7] J. S. Buck, W. H. Perkin, Jr., and T. S. Stevens, *ibid.*, 1471 (1925).

[8] All melting points are corrected. Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[9] J. J. Padbury and H. G. Lindwall, *J. Am. Chem. Soc.*, **67**, 1268 (1945).

was removed by distillation and 60 ml. of water added. Extraction of the basic solution with ether afforded an almost quantitative yield of III, which after several recrystallizations from a 1:3 mixture of benzene and low boiling (b.p. 30–60°) petroleum ether had m.p. 77–79° (lit.[6] m.p. 65°).

Anal. Calcd. for $C_{10}H_9NO$: C, 75.50; H, 5.70; N, 8.80. Found: C, 75.76; H, 5.77; N, 8.63.

Benzoic acid was obtained upon acidification of the alkaline solution remaining.

The phenylurethane derivative of III was obtained as a white crystalline solid from carbon tetrachloride, m.p. 148–150°.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.22; H, 5.29; N, 9.76.

Conversion of 1-Isoquinolylcarbinol (III) to 1-Methylisoquinoline.—A 2.0-g. portion of III was reduced[7] to 1-methylisoquinoline (0.51 g., 28.2%). This was characterized as its picrate, which after recrystallization from ethanol had m.p. 231–232° (lit.[10] m.p. 230–232°), and as its methiodide, which after recrystallization had m.p. 207–208° (lit.[10] m.p. 208°).

Hydrochloride of 2-Quinolylcarbinyl Benzoate (II).—This compound was prepared from 10.4 g. (0.04 mole) of 1-benzoyl-1,2-dihydroquinaldonitrile[11] in exactly the same manner as described above for the hydrochloride of I; 8.5 g. (72.1%) was obtained. Recrystallization from ethanol gave m.p. 107–109°.

Anal. Calcd. for $C_{17}H_{14}NClO_2$: C, 68.15; H, 4.79; N, 4.67; Cl, 11.83. Found: C, 67.78; H, 5.01; N, 4.48; Cl, 10.72.

2-Quinolylcarbinol (IV).—This compound was obtained in almost quantitative yield from the saponification of 4.0 g. (0.013 mole) of the hydrochloride of II in a manner analogous to that described above for III. Recrystallization from a 1:3 mixture of benzene and low boiling petroleum ether gave m.p. 65–67° (lit.[12] m.p. 66–68°).

The phenylurethane derivative of IV had m.p. 127–129° (lit.[12] m.p. 128–130°).

Acknowledgment.—The authors wish to thank the American Chemical Society Petroleum Research Fund for its support.

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The Preparation of Formic Benzoic Anhydride

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Received August 26, 1963

Although formic acetic anhydride may be prepared readily,[2] examination of the literature revealed no references to formic benzoic anhydride (I).

Formic benzoic anhydride has been prepared by the action of benzoyl chloride on a twofold excess of sodium formate in diethylene glycol dimethyl ether (DMC) or tetrahydrofuran (THF). The infrared spectrum of I in carbon tetrachloride solution showed carbonyl bands at 1785 and 1755 cm.$^{-1}$, in addition to strong bands at 1045 and 1020 cm.$^{-1}$. The proposed structure was confirmed by the neutralization equivalent of a hydrolyzed sample and by elemental analysis, although a slightly high value for carbon was obtained (presumably due to decomposition of I before analysis of the sample could be made). Reaction of I with aniline afforded both formanilide and benzoic acid in good yields. The formation of formanilide rather than benzoic acid anilide is analogous to the behavior of formic acetic anhydride.[2]

Although a small amount of I was isolated by distillation, there was extensive thermal decomposition. To obtain larger amounts of material, the reaction (in THF) was allowed to go almost to completion and was filtered from sodium chloride and unchanged sodium formate while there was still a small amount of benzoyl chloride present. The reaction could be followed conveniently by infrared. In this manner, formic benzoic anhydride, contaminated with small amounts of both benzoic acid (decomposition product of I) and benzoyl chloride, was obtained after removal of solvent.

If the reaction of sodium formate with benzoyl chloride was allowed to go to completion, formic benzoic anhydride was found to decompose in the reaction mixture to benzoic acid with the evolution of a gas (probably carbon monoxide). The infrared spectra of samples removed periodically throughout the reaction showed that this decomposition did not begin until essentially all of the benzoyl chloride had reacted. This suggests the possibility that small amounts of sodium formate dissolved in the reaction medium are catalyzing the observed decomposition.

Experimental[3]

Preparation of Formic Benzoic Anhydride.—To a stirred suspension of 80 g. (1.178 moles) of pulverized sodium formate in 100 ml. of dry DMC was added 82.8 g. (0.589 mole) of benzoyl chloride over a period of 65 min. (internal temperature 8–9°). After addition was complete, the mixture was stirred for 2.7 hr. at 9–15° and filtered under nitrogen. The infrared spectrum of the colorless filtrate showed bands at 1785, 1755, 1045, and 1020 cm.$^{-1}$, which were assigned to formic benzoic anhydride. There was no benzoic acid carbonyl, and it appeared that most of the benzoyl chloride had reacted. After the solution had stood overnight at room temperature, infrared analysis indicated that no decomposition had taken place. An aliquot of the above filtrate was distilled through a micro Vigreux column to yield 10.15 g. of formic benzoic anhydride, b.p. 64.5° (0.45 mm.)–69° (0.60 mm.). There was a white crystalline residue of 6.51 g., the infrared spectrum of which showed a strong benzoic acid carbonyl at 1695 cm.$^{-1}$. Infrared analysis showed the distillate to contain formic benzoic anhydride contaminated with a small amount of benzoic acid. Formic benzoic anhydride was purified by placing a small amount of the distillate in a sublimation apparatus and distilling the liquid at room temperature and high vacuum onto a cold finger cooled with ice–water. A sample of this purified material was hydrolyzed with water and a neutralization equivalent was obtained on the liberated acids.

Anal. Calcd. for $C_8H_6O_3$: C, 64.0; H, 4.03; neut. equiv., 75.06. Found: C, 64.8; H, 4.29; neut. equiv., 75.2

When a similar reaction mixture was not filtered from excess sodium formate but was stirred for 19.3 hr. at 19–37° after the completion of the benzoyl chloride addition, the infrared spectrum of the mixture showed a benzoic acid carbonyl at 1695 cm.$^{-1}$ and no trace of formic benzoic anhydride.

In THF, 100 hr. was required for the reaction of sodium formate (0.589 mole) with 0.294 mole of benzoyl chloride to go almost to completion. The temperature was varied from 0 to 53°, and the reaction was followed carefully by observing the disappearance of the 876-cm.$^{-1}$ band of benzoyl chloride in the infrared. The formic benzoic anhydride obtained after dilution of the reaction mixture with pentane, filtration, and removal of solvent from the filtrate was contaminated with only small amounts of benzoic acid and benzoyl chloride.

The reaction of I with aniline in ether solution afforded a 65.5% yield of formanilide, m.p. 43–49° (m.p. 47–50° after recrystn.), and a 74.5% yield of benzoic acid, m.p. 120–122°. Formanilide and benzoic acid were identified by their infrared spectra and by mixture melting points with authentic samples.

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(1) Northern Regional Laboratory, 1815 N. University St., Peoria, Ill.

(2) C. W. Huffman, *J. Org. Chem.*, **23**, 727 (1958), and references quoted therein.

(3) Melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer.