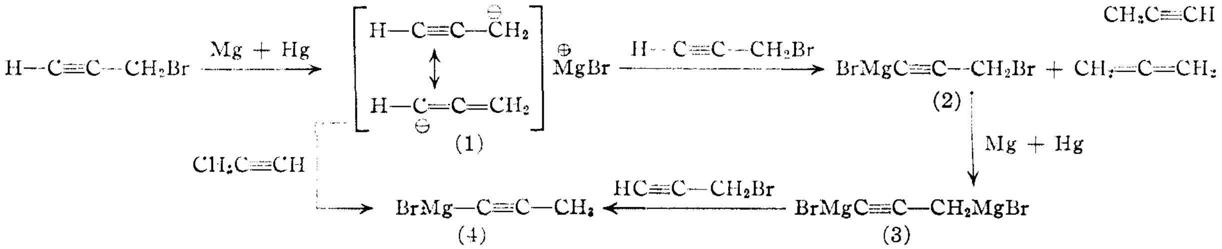
acid V and of 2-butynoic acid, $CH_3{-}C{\equiv}C{-}CO_2H$ (VI).[6] Aside from the mentioned band near 3270 cm.$^{-1}$, the spectrum contains a strong band near 2240 cm.$^{-1}$ characteristic of the triple bond conjugated with a carboxy group ($-C{\equiv}C{-}CO_2H$), and the strong 1950 cm.$^{-1}$ allenic bond ($C{=}C{=}C{-}$) absorption band. The positions and intensities of the mentioned bands are consistent with the ones of similar compounds previously described.[1,7]

The formation of the found acids could be explained on the basis of the equations



Acids derived from forms 2 and 3 are not isomeric with the one derived from forms 1 and 4. Their presence or absence was not established as only a product boiling over a limited range was analyzed. The presence of the Grignard reagent 3 in the reaction product of propargyl bromide and magnesium was favored by Gaudemar[8] who also found glycols of the type $R{-}CHOH{-}C{\equiv}C{-}CH_2{-}CHOH{-}R$ in the reaction product of "propargylmagnesium bromide" and aldehydes.

On the basis of our findings, we conclude that the French workers[4] were dealing with an impure sample of IV and that they were incorrect in thinking that V is unstable. Since we were not successful in separating V from IV and VI we were not able to characterize this compound.

Experimental

Propargyl bromide was prepared from propargyl alcohol[9] and phosphorus tribromide in the presence of pyridine. Since there are several different constants recorded in the literature, we rectified the bromide through a column till a constant boiling point and refractive index were reached; b.p. 81°, $n^{25}D$ 1.4875.

Anal.[10] Calcd. for C_3H_3Br: C, 30.2; H, 2.5. Found: C, 30.2; H, 2.6.

Preparation and Carbonation of the Grignard Reagent.—A solution of 36 g. (0.3 mole) of propargyl bromide in 300 ml. of dry ether reacted with amalgamated magnesium as previously described.[1] A solid which adhered to the side of the boiler separated during this reaction and was loosened with a spatula before the ether solution (suspension) was poured upon a Dry Ice–ether mixture and allowed to come to room temperature overnight. The hydrolysis with a saturated solution of ammonium chloride was accompanied by an evolution of a gas. The acidic portion (7 g., 28% yield) was dark colored. On a one-plate distillation, 4 g. (b.p. 75 to 80° at 5 mm.) of a colorless semi-solid was collected. On four crystallizations from a mixture of petroleum ether (30–60°) and benzene, a product comprising 2.5 g. of white plates was isolated, m.p. 83–84°.

Anal. Calcd. for $C_4H_4O_2$: C, 57.1; H, 4.8. Found: C, 56.8; H, 4.9.

Its infrared spectrum[11] in Nujol is described by curve A in Fig. 1. The mother liquor was redistilled and the portion boiling at 67–68° at 4 mm. partly solidified. The solid was removed by filtration and the filtrate analyzed.

Anal. Calcd. for $C_4H_4O_2$: C, 57.1; H, 4.8. Found: C, 56.7; H, 5.3.

Its infrared spectrum is described by curve B in Fig. 1.

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[6] W. L. German, G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1604 (1937), list it to melt at 76–78°.

[7] J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949).

[8] M. Gaudemar, *Compt. rend.*, **233**, 64 (1951).

[9] We gratefully acknowledge the General Aniline and Film Co. for their generous sample.

[10] Microanalyses by the Microanalytical Laboratory of the University of Pittsburgh.

[11] Infrared analyses by Dr. F. A. Miller and co-workers at the Mellon Institute, Pittsburgh, Pa.

CONTRIBUTION NO. 833 FROM THE
DEPARTMENT OF CHEMISTRY
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1-Nitromethylcyclohexanol and Homologs

BY THOMAS F. WOOD AND RICHARD J. CADORIN

Recently there have appeared four papers by different investigators[1–4] in which the preparation of 1-nitromethylcyclohexanol from the condensation of nitromethane and cyclohexanone by several methods is described. This compound was first prepared and described by Fraser and Kon[5] in 1934. Since that time other investigators[1,4,6] have encountered difficulties in reproducing the results of these workers. Nightingale and coworkers[1] advocated the use of freshly prepared sodium ethoxide catalyst for carrying out the condensation which was conducted at 50° for 1.5 hours and 36 hours at room temperature; they reported a yield of 33.7% by this modification in contrast to the 45% yield claimed by Fraser and Kon.[5] Grob and von Tscharner[2] satisfactorily effected the condensation of nitromethane and cyclohexanone at room temperature in absolute alcohol using a molar equivalent of sodium ethoxide as condensing agent and with exclusion of moisture; after the mixture was allowed to stand overnight the insoluble sodium salt of the resulting nitroalcohol was isolated and decomposed with acetic acid to yield the desired nitroalcohol in 75% yield. Dauben and co-workers[4] mentioned the difficulties encountered by others[1,6] in effecting the condensation and described a slight improvement in yield (78 to 82%) by the use of a 50% excess of nitromethane in the Grob–von Tscharner procedure.[2] This improved yield was apparently calculated on either the sodium ethoxide or the cyclohexanone used. They further summarized their experiences

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[1] D. V. Nightingale, F. B. Erickson and N. C. Knight, *J. Org. Chem.*, **15**, 782 (1950).

[2] C. A. Grob and W. von Tscharner, *Helv. Chim. Acta*, **33**, 1070 (1950).

[3] G. A. R. Kon, *J. Chem. Soc.*, 843 (1951).

[4] H. J. Dauben, Jr., H. J. Ringold, R. H. Wade and A. G. Anderson, Jr., THIS JOURNAL, **73**, 2359 (1951).

[5] H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934).

[6] H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 384 (1943).

using as condensing agents one equivalent of sodium methoxide in methanol (yield 42%) and potassium *t*-butoxide in *t*-butanol (38% yield) and attributed the lowered yields to the greater solubilities of the condensation product salts in the respective solvents; diethylamine was also found to be an effective condensing agent for the preparation of 1-nitromethylcyclohexanol in contrast to earlier results[5,6] giving yields of 45–54% under the proper conditions. The note recently published by Kon,[3] apparently in response to the communication of Nightingale and co-workers,[1] mentions the troubles reported by other workers[1,6] in repeating the preparation of 1-nitromethylcyclohexanol by the method originally published.[5] Kon admitted that the original results could not always be attained and was unable to account for the discrepancy. He then described what he considered to be the optimum conditions for carrying out the condensation, reporting a yield of 47%. In the prior literature on the preparation of 1-nitromethylcyclohexanol, which has been summarized above, there is nothing to suggest the source of irreproducibility in the method of Fraser and Kon.[5]

In view of the continuing interest in the preparation of 1-nitromethylcyclohexanol as evidenced by recent publications[1–4] it was deemed worthwhile to record the results obtained in these laboratories. It was desired to prepare a considerable amount of this compound. In agreement with the results of others[1,3,4,6] it was found that the method originally described by Fraser and Kon[5] was not dependable; by this method fair results (35%) were obtained in only one run of four attempted; in the others the yield was zero. By a modification of their procedure there were conveniently prepared considerable amounts of the nitroalcohol. Yields of around 50% of theory, calculated on the initial nitromethane, were consistently obtained using redistilled commercial nitromethane, commercial cyclohexanone, a catalytic amount of sodium hydroxide solution as condensing agent and enough methanol to maintain homogeneity. The condensation was conducted at 17–20° for 4–6 hours and then the sodium hydroxide neutralized with acetic acid, using a slight excess of acid. The crude product was washed with water and vacuum distilled. In several runs some crystalline salt was observed in the solution during the condensation but no deviation in yield was encountered in these cases. The method has given consistently good results in twelve test batches of the size described below. Results were equally satisfactory when nitromethane was condensed with *m*- and *p*-methylcyclohexanone. With nitroethane and cyclohexanone the yields were lower (20–23%).

It has been determined that under the conditions chosen a sufficient time of condensation for nitromethane and cyclohexanone is between 4 to 6 hours where yields are 50 to 51% of theory. A 10-hour run gave a yield of 47%. It was not determined whether long condensation periods would lower the yield still further. The reaction proceeds fairly rapidly at room temperature and is mildly exothermic requiring occasional cooling with ice-water to keep the temperature just below 20°. In test condensations the yields were determined after 1, 2 and 3 hours and found to be 42.3, 47.8 and 49%. Thus, the reaction proceeds rapidly to equilibrium when all the reactants are in solution.

The yields given are calculated on the nitromethane with no adjustment made for recovered starting materials. If Kon's[3] yield is figured on this basis, it amounts to only 37.8% of theory rather than the 47% given; he does not state whether his yield is calculated on nitromethane or cyclohexanone consumed. If an effort had been made to recover unconverted starting materials and yields figured on materials actually consumed, our yield percentagewise would have been considerably higher. The method does offer some advantages over the procedure of Grob and von Tscharner, even though the conversion is lower, in that it does not require the use of absolute alcohol, sodium ethoxide and anhydrous conditions; the necessity of filtering off the sodium salt of the condensation product is avoided; this would eliminate an expensive step on a technical scale.

The question regarding the source of irreproducibility of the original results of Fraser and Kon[5] remains. It is believed that the difficulties of previous workers in following the original method may be due to traces of alkali in the crude nitroalcohol during the distillation, causing the compound to decompose into the starting materials. In this case the wash with sodium bicarbonate as given in the original procedure may be harmful since traces of bicarbonate would decompose to carbonate during the distillation. It seems probable that such difficulty would be encountered when the crude was insufficiently dried before distillation. In order to determine whether traces of bicarbonate would actually cause decomposition of the crude nitroalcohol during distillation, a run was made using the standard condensation conditions and the crude given a final wash with 5% sodium bicarbonate solution. When this crude was distilled in the usual way there was observed decomposition of the still contents and the yield was zero; the distillation proceeded to a dry still pot without any of the nitroalcohol distilling. The distillate was mainly cyclohexanone while most of the nitromethane went into the vacuum line. Another experiment was run in which there was added 6 drops of glacial acetic acid to the crude nitroalcohol; in this case the distillation was normal and a yield of 50% was obtained.

Experimental

1-Nitromethylcyclohexanol.—Into a solution of 91.5 g. of redistilled commercial nitromethane (1.5 moles) (Commercial Solvents Corp.), 196 g. of commercial cyclohexanone (2.0 moles) (du Pont) and 125 g. of methanol, cooled to 17°, was added with good stirring a solution of 4 g. of sodium hydroxide, 8 g. of water and 30 g. of methanol over a 30-minute period with the temperature kept below 20° during the addition. The condensation was mildly exothermic. The solution was stirred for 6 hours at 15–20°. The condensation mixture was usually homogeneous throughout the reaction and at the end was reddish-yellow in color and faintly cloudy. In a few runs there was noticed some crystalline salt suspended in the solution up until it was acidified with acetic acid but no deviation in yield was noticed in these cases. The solution was cooled to 15° and neutralized with a solution of 6 g. of glacial acetic acid in 50 g. of water. The batch was poured into 400 ml. of water and shaken. The bottom oil layer which separated amounted to 270 g. The oil was washed again with 250 ml. of water saturated with salt. The crude oil (232 g.) was directly vacuum distilled yielding 100 g. of low boiling material, b.p. 38 to 93° (63 to 2 mm.). The desired product then was obtained, b.p. 93–95° (2 mm.), as an almost colorless slightly viscous oil of mild odor amounting to 121.5 g. (51%), d^{20}_4 1.1579, n^{20}_D 1.4875. There was no residue.

Anal. Calcd. for $C_7H_{13}O_3N$: C, 52.8; H, 8.18; N, 8.82. Found: C, 52.9; H, 8.5; N, 8.9.

Another condensation was run in exactly the same fashion as described above except that a final wash with 100 g. of 5% sodium bicarbonate solution was given before distillation. On distillation the entire product distilled at 54–60° (27 mm.) (pot to 130° at end) leaving no residue in the still. There was evidence of decomposition as soon as the pot temperature reached 85°. The distillate was mainly cyclohexanone. Most of the nitromethane was volatilized into the vacuum line.

Another condensation was run in the regular manner. The crude product after a wash with 250 ml. of water saturated with salt amounted to 240 g. There was added 6 drops of glacial acetic acid with good stirring and the oil vacuum distilled yielding 107 g. of low boiling material, b.p. 35 to 87° (65 to 1.5 mm.). The 1-nitromethylcyclohexanol then was obtained, b.p. 86–87° (1.5 mm.), 120 g. (50% of theory).

1-Nitromethyl-*m*-methylcyclohexanol.—This compound was prepared in exactly the same manner as the first procedure above using 224 g. (2 moles) of *m*-methylcyclohexanone (Eastman Kodak Company). The 1-nitromethyl-*m*-methylcyclohexanol was obtained as a colorless liquid, b.p. 95° (1.5 mm.), d^{20}_4 1.1120, n^{20}_D 1.4810. The yield was 49.0% calculated on the nitromethane used (1.5 moles).

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.1. Found: N, 8.3.

1-Nitromethyl-*p*-methylcyclohexanol.—By the same procedure this compound was obtained with a yield of 53.6% calculated on the nitromethane used (1.5 moles). The product distilled at 98–99° (1.5 mm.) as a pale yellow liquid, slightly viscous, and of mild odor, d^{20}_4 1.1115, n^{20}_D 1.4818. On standing this compound solidified to a white solid, f.p. 31–32°.

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.1. Found: N, 8.4.

1-Nitroethylcyclohexanol.—This compound was prepared by the above general procedure by condensing 112.5 g. (1.5 moles) of nitroethane with 2 moles of cyclohexanone. The product was obtained as a pale yellow, slightly viscous liquid, b.p. 84–87° (1.5 mm.), d^{20}_4 1.1260, n^{20}_D 1.4840. The yield was 58.5 g. (22.6% of theory).

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.1. Found, N 8.4.

RESEARCH LABORATORIES
THE GIVAUDAN CORPORATION
DELAWANNA, N. J.

RECEIVED APRIL 30, 1951

NEW COMPOUNDS

Oxidation Products of 8-Chloro-1,3-Benzodioxan-6-hydroxymethyl-7-carboxylic Acid Lactone

5-Hydroxy-6-chloro-1,2,4-tricarboxylic Acid.—8-Chloro-1,3-benzodioxan-6-hydroxymethyl-7-carboxylic acid lactone,[1] 5 g., was dissolved in 250 ml. of water containing 10 g. of potassium hydroxide at 80° and a warm solution of 7.5 g. of potassium permanganate in 250 ml. of water was added with stirring over a period of 20 minutes. After filtration, the filtrate was cooled to room temperature, acidified and extracted with an equal volume of ether. The ethereal solution was evaporated to 100 ml. and 200 ml. of benzene was added, after which the volume was reduced to 100 ml. by heating. Cooling gave 3.2 g. of white solid. Several crystallizations from 50% formic acid produced white crystals, m.p. 243.0–243.5°. The compound gives a dark red color with aqueous ferric chloride.

Anal. Calcd. for $C_9H_5ClO_7$: Cl, 13.61. Found: Cl, 13.61, 13.72.

8-Chloro-1,3-benzodioxan-6,7-dicarboxylic Acid.—The lactone, 20 g., was dissolved in 1 l. of water containing 40 g. of potassium hydroxide at a temperature of 85° and a warm solution of 30 g. of potassium permanganate in 1 l. of water was added over a period of 20 minutes, the temperature being maintained at approximately 75°. After the permanganate had been reduced, the mixture was filtered and the filtrate was cooled to room temperature and acidified. Extraction with ether and evaporation of the ethereal layer gave a slightly colored solid which was dissolved in 100 ml. of water by boiling. The color was removed by activated charcoal and the filtrate was placed in the refrigerator overnight, after which period 6 g. of a white, voluminous precipitate, m.p. 167–170°, formed. One crystallization from water and two by solution in hot acetone followed by the addition of ligroin gave 3.3 g. of white crystals, m.p. 182.0–182.8°.

Anal. Calcd. for $C_{10}H_7ClO_6$: C, 46.44; H, 2.73; Cl, 13.71. Found: C, 46.18, 46.28; H, 2.54, 2.53; Cl, 13.67.

DEPARTMENT OF CHEMISTRY
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KNOXVILLE, TENNESSEE
C. A. BUEHLER
ROY L. PRUETT

RECEIVED JULY 16, 1951

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[1] C. A. Buehler, James O. Harris, Comer Shacklett and Burton P. Block, THIS JOURNAL, **68**, 577 (1946).

3-Chloro-4-hydroxyphthalic Acid and its Derivatives

3-Chloro-4-methoxyphthalic Acid.—6-Methoxy-7-chlorophthalide,[1] 10 g., and 7 g. of potassium hydroxide were dissolved in 200 ml. of water at 80°. This solution at 50° was treated with a solution of 15 g. of potassium permanganate in 600 ml. of water, also at 50°, over a 30-minute period while the temperature was maintained at 50–55°. After standing for 2 hours, the mixture was filtered and the excess of permanganate was destroyed with sodium bisulfite. Filtration followed by acidification gave a solution which was extracted with an equal volume of ether. The ethereal solution was evaporated down to 100 ml. and then 100 ml. of benzene was added. Additional concentration to 75 ml. and cooling gave a white precipitate, 7.7 g., m.p. 181–183°, with loss of water. Two crystallizations from glacial acetic acid produced white needles, m.p. 184.5–185.0° although the value varies somewhat with the rate of heating.

Anal. Calcd. for $C_9H_7ClO_5$: C, 46.87; H, 3.06; Cl, 15.38; CH_3O, 13.46; neut. equiv., 116. Found: C, 46.80, 46.76; H, 2.78, 2.90; Cl, 15.41, 15.23; CH_3O, 13.33; neut. equiv., 116, 117.

3-Chloro-4-methoxyphthalic Anhydride.—3-Chloro-4-methoxyphthalic acid, 2 g., was heated at 190° in an oil-bath to give 1.7 g. of white solid. Crystallization from glacial acetic acid produced white crystals, m.p. 172.5–173.0°.

Anal. Calcd. for $C_9H_5ClO_4$: Cl, 16.68. Found: Cl, 16.62, 16.61.

3-Chloro-4-methoxyphthalimide.—The anhydride, 1.7 g., was mixed with an equal weight of urea and heated to 150°. Ammonia was evolved for about 10 minutes and then the liquid solidified. Crystallization from methanol gave 1.2 g. of a white, fluffy solid which after one more crystallization melted at 310.0–311.0°.

Anal. Calcd. for $C_9H_6ClNO_3$: Cl, 16.76; N, 6.62. Found: Cl, 16.69, 16.84; N, 6.56, 6.56.

3-Chloro-4-hydroxyphthalic Acid.—3-Chloro-4-methoxyphthalic acid, 2.3 g., was refluxed for 15 hours with 100 ml. of 48% hydrobromic acid to produce 1.7 g. of slightly brown needles, m.p. 206–207°. Crystallization from 85% formic acid gave white needles, m.p. 210.0–210.5°.

Anal. Calcd. for $C_8H_5ClO_5$: Cl, 16.37. Found: Cl, 16.32, 16.34.

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