A sample of the diketo acid was heated for thirty minutes with a 15% potassium hydroxide solution. γ-Benzoylbutyric acid (m. p. 126–127°) was isolated from the reaction mixture. The acid was identified by comparison with an authentic specimen.

Synthesis of Ethyl γ,γ-Dibenzoylbutyrate.—This ester was obtained in two ways—by esterification of the acid and by the condensation of ethyl β-chloropropionate with dibenzoylmethane. The latter process was carried out according to the following procedure. To a cold solution of 1 g. of metallic sodium in 30 cc. of absolute ethyl alcohol was added, with stirring, 10 g. of dibenzoylmethane. After the mixture had become homogeneous 8.7 g. of ethyl β-chloropropionate was added gradually. The mixture was allowed to stand, with occasional stirring, for eighty-six hours. The product, after recrystallization from alcohol, melted at 95–95.5°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.0; H, 6.2. Found: C, 74.2; H, 6.3.

Synthesis of the Oxide (VII).—Two grams of 1-phenyl-5-benzoyl-1-cyclopentene was dissolved in chloroform containing the theoretical amount of perbenzoic acid. After twenty-four hours the chloroform solution was washed with aqueous sodium bicarbonate and allowed to evaporate. The solid residue when recrystallized from ethyl acetate melted at 169–169.5° and when mixed with a sample of the oxide described above caused no lowering of the melting point.

Summary

The action of zinc (in acetone) on 1,4-dibromo-1,4-dibenzoylbutane gives rise to a mixture of products of which the principal is 1-phenyl-5-benzoyl-1-cyclopentene oxide (VII). The corresponding pentene (V) and 1,4-dibenzoylbutane are also formed. Structure proofs are presented for V and VII.

A mechanism which involves an intramolecular Reformatsky condensation is suggested to explain the formation of the two cyclic compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

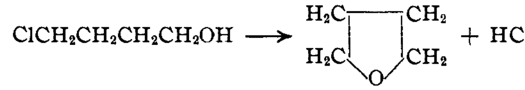
Reduction of Furan and the Preparation of Tetramethylene Derivatives

BY DONALD STARR[1] AND R. M. HIXON

A convenient method for the preparation of δ-chlorovaleronitrile was desired in order that the reaction developed for the α-substituted pyrrolines and pyrrolidines[2] could be used for the synthesis of the α-substituted tetrahydropyridines and piperidines. In spite of the large number of investigations leading to the preparation of various tetramethylene derivatives, no reference to δ-chlorovaleronitrile could be found in the literature.

Tetramethylene bromide and bromohydrin have previously been prepared from tetrahydrofuran,[3] which should be a more convenient source of tetramethylene derivatives than its analog, pyrrolidine.[4] The practicability of using tetrahydrofuran for the synthesis of δ-chlorovaleronitrile depended upon finding an efficient method for reducing furan.[3,5] The catalytic reduction using platinic oxide-platinum black catalyst[6] was found to be very unsatisfactory, but palladous oxide-palladium black[7] made possible a quantitative conversion of furan to tetrahydrofuran.

Tetramethylene chlorohydrin[8] has been reported as being unstable when distilled at temperatures appreciably above 85°. Presumably, the reaction is



This reaction has been studied in the reverse direction to determine its applicability in the preparation of tetramethylene chlorohydrin. The splitting of tetrahydrofuran with hydrogen chloride was studied first in the vapor phase since the partial pressure of the tetramethylene chlorohydrin was so much less than that of the tetrahydrofuran that there was slight probability of a secondary reaction occurring to form tetramethylene chloride. Experience showed that there was very little difference in the yield of chlorohydrin if the reaction occurred in the liquid phase. The reaction in the liquid phase is about three times as rapid as in the gaseous phase. The compound partially breaks down at about 106° in both cases,

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(1) Research Fellow, Rockefeller Fluid Research Fund.

(2) Craig, Bulbrook and Hixon, THIS JOURNAL, **53**, 1831 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).

(3) Bouguignon, *Bull. soc. chim. Belg.*, **22**, 87 (1908).

(4) Von Braun and Besche, *Ber.*, **39**, 4119 (1906).

(5) Smyth and Walls, THIS JOURNAL, **54**, 3231 (1932). Furan was reduced catalytically in butyl alcohol but no details were reported.

(6) "Organic Syntheses," Vol. VIII, p. 92.

(7) Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

(8) Bennett and Heathcoate, *J. Chem. Soc.*, 268 (1929); Kirner and Richter, THIS JOURNAL, **51**, 2503 (1929).

even in the presence of an atmosphere of hydrogen chloride.

Experimental Part

Furan was prepared by the decarboxylation of furoic acid[9] in the presence of copper sulfate and crude tar bases. Purification was necessary in order to obtain satisfactory reduction. The compound was dried over calcium chloride and fractionated before each reduction. Nearly all of the material distilled at 31–32°.

Tetrahydrofuran was obtained by the reduction of furan in the presence of palladous oxide-palladium black[7] with a hydrogen pressure of seven atmospheres, using an apparatus similar to that of Adams and Voorhees.[10] Similar experiments with platinic oxide-platinum black catalyst[6] were unsuccessful.

The reduction proceeded smoothly and quantitatively in the absence of any solvent after an initial time lag of five to ten minutes. The reduction of 0.1 mole using 0.2 g. of palladous oxide required forty to fifty minutes, but the catalyst gradually became inactive with the addition of two more 0.1-mole portions of furan. The following procedure was used for the preparation of larger amounts of tetrahydrofuran. With 0.2 g. of catalyst, 10 g. of furan was reduced and then 20 g. of furan with another 0.2 g. of catalyst was added. As the reduction neared completion, three successive portions of 30 g. of furan with 0.2 g. of catalyst, were added. The entire reduction of the 120 g. required eighteen to twenty hours and 1.0 g. of palladous oxide. The recovery was 95% of the theoretical with the entire quantity distilling at 64–66°, n^{25}_{D} 1.4040. The loss of 5% was probably due to the volatility of furan during the sweeping of the reduction bottle with hydrogen. A solution of furan in absolute or in 95% alcohol can be reduced more rapidly than can furan without a solvent, but it is not possible to separate the tetrahydrofuran from the alcohol in satisfactory yields.

Tetramethylene Chlorohydrin.—Hydrogen chloride gas was bubbled through 114 g. of boiling tetrahydrofuran in a flask fitted with a reflux condenser and a thermometer dipping in the boiling liquid. The reaction was stopped when the temperature reached about 106°, and the mixture fractionated. Three fractions were collected, 20.6 g. of a low boiling fraction which was about 95% tetrahydrofuran, 75.7 g. of tetramethylene chlorohydrin boiling at 80–90° (14 mm.) or 56% of the theoretical yield calculated on the tetrahydrofuran consumed, and 5.5 g. of a fraction distilling at 140–149° (14 mm.), which was not further investigated. Refractionation of the chlorohydrin yielded a fraction boiling at 81–82° (14 mm.). The identity of the tetramethylene chlorohydrin was confirmed by its α-naphthylurethan,[8] m. p. 69°.

Tetramethylene Chlorobromide.—Two moles of tetramethylene chlorohydrin were converted to tetramethylene chlorobromide by treatment with one mole of phosphorus tribromide, analogous to the preparation of the trimethylene chlorobromide.[11] The yield was 98% of the theoretical. The pure compound gave the following constants: b. p. 175–176°, n^{20}_{D} 1.4885, d^{20}_{4} 1.488, MR_D 33.23, MR_D calcd. 33.30. Calculated for C_4H_8ClBr: C, 28.0; H, 4.70. Found: C, 27.9; H, 4.64.

δ-Chlorovaleronitrile was prepared according to the directions for γ-chlorobutyronitrile[12] except that the mixture was refluxed gently overnight. A small quantity of the same compound was prepared by refluxing tetramethylene chloride and sodium cyanide in 50% alcohol for fifteen hours. The δ-chlorovaleronitrile of b. p. 100–110° (16 mm.) was obtained in 52% yield from the tetramethylene chlorobromide. A fraction boiling at 101–102° (16–17 mm.) gave the following constants: n^{25}_{D} 1.4441; d^{25}_{4} 1.061, MR_D 29.4, calcd. MR_D 29.98. Calculated for C_5H_8NCl: N, 11.91. Found: N, 11.98, 12.18.

The δ-chlorovaleronitrile was characterized by converting it to α-substituted six-membered nitrogen heterocyclic compounds. Phenylmagnesium bromide when treated with δ-chlorovaleronitrile yielded α-phenyltetrahydropyridine[13] which was identified by the picrate of m. p. 181.5° and the hydrochloride, m. p. 86°. The corresponding methyl compound has also been made. The details of these syntheses will be published later with a series of similar compounds.

Summary

Furan has been reduced quantitatively to tetrahydrofuran using palladous oxide-palladium black catalyst.

Tetramethylene chlorohydrin was prepared by splitting tetrahydrofuran with gaseous hydrogen chloride.

Tetramethylene chlorobromide and δ-chlorovaleronitrile have been reported for the first time.

AMES, IOWA

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[9] Gilman and Lousinian, *Rec. trav. chim.*, **52**, 156 (1933).

[10] "Organic Syntheses," Vol. VIII, p. 10.

[11] Cloke, *et al.*, THIS JOURNAL, **53**, 2794 (1931).

[12] "Organic Syntheses," Vol. VIII, p. 52.

[13] Gabriel, *Ber.*, **41**, 2012 (1908).