Reaction of 3,4-Dihydro-2,5-dimethyl-2H-pyran-2-carboxaldehyde (Methacrolein Dimer) with Molecular Oxygen

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In the presence of cobalt and nickel salts, 3,4-dihydro-2,5-dimethyl-2H-pyran-2-carboxaldehyde is cleaved by molecular oxygen to yield 2,5-hexanedione. Both acetic and formic acids are by-products, and large amounts of polymer are also formed. When the reaction is run in *t*-butyl alcohol, hydrolysis of the product mixture yields *p*-cresol. A related compound, 5,6-dihydro-2,6-dimethyl-2H-pyran-3-carboxaldehyde, can be cleaved by oxygen at higher temperatures, but only acetic acid and tar were found.

A SAMPLE of 3,4-dihydro-2,5-dimethyl-2H-pyran-2-carboxylic acid (I) was needed recently. The corresponding aldehyde (II) can be prepared by the Diels-Alder dimerization of methacrolein (*3*), and oxidation to I has been achieved with silver oxide in dry benzene (*4*). In a search for a simpler method, II was reacted with molecular oxygen, using cobalt and nickel salts as catalysts. Similar conditions have been employed for the oxidation of methacrolein to methacrylic acid (*1*). In this case, however, the desired acid (I) was not obtained—the major identifiable products were 2,5-hexanedione (III), (20 to 30% yield), acetic acid (15 to 25%), and formic acid (15%). Traces of water and substantial quantities of polymer were produced in every run.

When II was oxidized in *t*-butyl alcohol, at least four additional products were observed, but could not be separated in a pure state, even by preparative gas chromatography. Concentration of the reaction mixture and a brief reflux with dilute hydrochloric acid yielded *p*-cresol (7% yield). No *p*-cresol could be isolated when benzene was the solvent, or when no solvent was used. No *o*- or *m*-cresol or other phenols could be detected in any of the runs. As yet, the course of this aromatization has not been determined.

An analogous compound, 2,6-dimethyl-5,6-dihydro-2H-pyran-3-carboxaldehyde (crotonaldehyde dimer) (IV) was oxidized in *t*-butyl alcohol at 65° and 125° C. At 65° C., no cleavage products were observed—oxygen uptake was rapid and exothermic, to yield the corresponding acid V. Treatment of the concentrated reaction mixture with dilute acid failed to produce any phenolics. At 125° C. cleavage did occur, but the only identified product was acetic acid (65% yield, assuming one mole of acid formed from one mole of IV). The rest was intractable tar. These results are summarized in Figure 1.

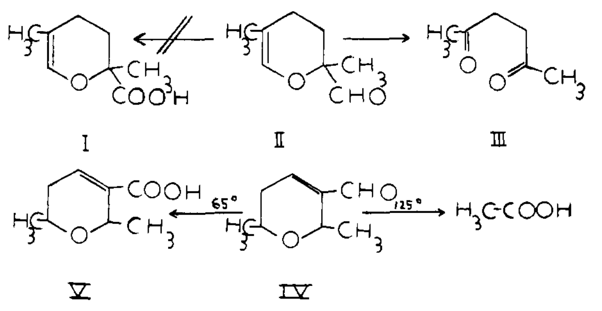

Figure 1. Catalytic oxidation of dihydro-2H-pyran-carboxaldehydes

EXPERIMENTAL

3,4-Dihydro-2,5-dimethyl -2H- pyran -2- carboxaldehyde (II) was prepared by the thermal dimerization of methacrolein at 175° C. (*3*). Purity (by gas chromatography) was 98% or better. Gradual decomposition was noted, and it is recommended that experiments with II be carried out within a week of preparation.

5,6-Dihydro-2,6-dimethyl -2H- pyran -3- carboxaldehyde (IV) was prepared by the autocondensation of crotonaldehyde in refluxing hydrochloric acid (*2*). Both *cis*- and *trans*-IV are formed by this reaction, and the mixture was used without separation.

Benzene, *t*-butyl alcohol, and cobalt and nickel acetates were obtained from commercial sources and used without further purification.

Product identification was by preparative gas chromatography on a Carbowax 4000 dioleate column. Acetic and formic acids, III, and *p*-cresol are well-known compounds, and identification from spectral and physical data was routine.

The following experiments are representative:

2,5-HEXANEDIONE (III). A mixture of 85.8 grams (0.61 mole) of II, 0.3 gram of cobalt (II) acetate tetrahydrate, and 0.3 gram of nickel acetate tetrahydrate was heated to 60° C. in a 300-ml. Magne-Drive autoclave under a pressure of 500 p.s.i.g. of oxygen. After five hours, when oxygen uptake had ceased, the autoclave was depressurized, and the contents distilled at atmospheric pressure. After a forerun of acetic and formic acids, 20 grams (0.18 mole, 29.5% yield) of 2,5-hexanedione, b.p. 192° C., were collected. The forerun was analyzed by gas chromatography. Yields of 5.5 grams (0.09 mole, 14.9%) of acetic acid and 4.0 grams (0.09 mole, 14.9%) of formic acid were obtained. A substantial amount (60 grams) of polymeric material was left after distillation. Attempts to characterize this material were unsuccessful—the infrared spectrum showed ether, hydroxyl, ketone, and ester linkages.

p-CRESOL. *p*-Cresol was prepared as follows. The reaction mixture from the oxidation of II in *t*-butyl alcohol was distilled to remove most of the solvent and lower-boiling components. The residue was refluxed 5 minutes with $2N$ aqueous hydrochloric acid, cooled, and extracted with benzene. The *p*-cresol was separated, and the yield determined by thin-layer chromatography.

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Reactions of *p*-Nitrotoluene Carbanion

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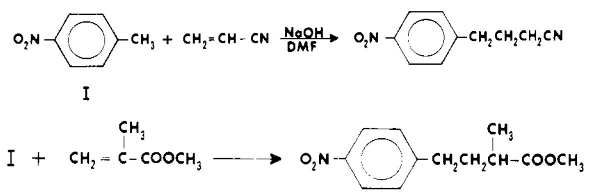
p-Nitrotoluene carbanion adds to acrylonitrile and methyl methacrylate to give 4-(4-nitrophenyl)butyronitrile and methyl 2-methyl-4-(4-nitrophenyl)butyrate, respectively.

ADDITION reactions of *p*-nitrotoluene carbanion have been impaired for the most part by the facile oxidation (*8, 9, 10*) and dimerization (*2, 3, 8, 9*) of the anion. Reactions with aldehydes have resulted in low yields of product, at best, and in most cases the only significant product has been the dehydrodimer, 4,4′-dinitrobibenzyl, or 4,4′-dinitrostilbene (*2–5*). The addition to aryl aldehydes can be directed to give good yields of product if conducted in polar aprotic solvents, such as dimethylformamide and dimethylacetamide (*6*).

This reaction has been extended to the addition of *p*-nitrotoluene carbanion to the activated double bonds of such substrates as acrylonitrile and methyl methacrylate. The addition proceeds readily, though in low yield, at room temperature to afford the 1 to 1 adducts, as well as higher molecular weight products.



The reactions occur to a reasonable extent at room temperature with sodium hydroxide catalysis and are sufficiently fast to compete with the known dimerization of the anion (*2, 3, 8, 9*) and the homopolymerization of acrylonitrile and methyl methacrylate (*7*). Whether or not the reactions are reversible under these conditions, as was established for the aldehyde adducts, has not been determined as yet.

EXPERIMENTAL

4-(4-Nitrophenyl)butyronitrile. A 250-ml. 3-necked flask fitted with magnetic stirrer, thermometer, and reflux condenser was charged with 27.4 grams (0.2 mole) of *p*-nitrotoluene and 40 ml. of dimethylformamide (DMF). To the resulting greenish yellow solution was added, under nitrogen and with stirring, 0.6 gram (0.015 mole) of freshly ground sodium hydroxide. To the red solution was added 10.4 grams (0.2 mole) of acrylonitrile in 35 ml. of DMF over a 1-hour period. After 2 hours, 1.5 ml. of concentrated (36%) hydrochloric acid was added and the solution filtered. Evaporation of solvent under reduced pressure gave a dark red semisolid residue. Treatment with hot chloroform gave 15.5 grams of insoluble light orange solid, m.p. 105° to 125° C.—higher molecular weight products from *p*-nitrotoluene and acrylonitrile. The red chloroform extract was evaporated under vacuum to a red oil, which was extracted with hot petroleum ether to remove the unreacted *p*-nitrotoluene. The 6.5 grams of red oily residue was distilled at 169–73° C. and 1.0 to 0.6 mm. (*1*) of Hg to yield 1.3 grams of substantially pure 4-(4-nitrophenyl)butyronitrile; IR (neat), 4.4μ (CN), 6.55 and 7.39μ (NO_2); NMR ($CDCl_3$), δ = 8.13 and 7.35 (2d, 4, ArH), 3.05–1.90 (m, 6, CH_2).

Hydrolysis of 0.7 gram of this liquid with 3.5 ml. of concentrated sulfuric acid and 3.0 ml. of water at reflux for 0.5 hour gave 0.66 gram of a white solid, 4-(4-nitrophenyl)butyric acid, which had m.p. 92–3° C. (*11*) on recrystallization from toluene.

Methyl-2-methyl-4-(nitrophenyl)butyrate. Thirteen and seven-tenths grams (0.1 mole) of *p*-nitrotoluene, 10.01 grams (0.1 mole) of methyl methacrylate, and 50 ml. of DMF were charged into a 250-ml. 3-necked flask fitted with a nitrogen inlet tube, magnetic stirrer, thermometer, and reflux condenser at room temperature. To the light yellowish green solution was added under nitrogen 1.0 gram (0.025 mole) of freshly ground sodium hydroxide. The reaction turned a vivid green initially, and after 1 hour a dark blue color formed. The reaction solution was acidified with 125 ml. of a 5% hydrochloric acid solution, whereupon a red oil separated from the mixture. The reaction mixture was extracted with three 50-ml. portions of benzene. The extracts were combined and dried over magnesium sulfate, and the solvent was vacuum-evaporated with water and oil pumps to 12.01 grams of a red oil, which started to crystallize at room temperature. After removal of most of the unreacted *p*-nitrotoluene by distillation at 90–5° C. and 0.25