

Lithium-Ammonia Reduction of 3-Furoic Acid

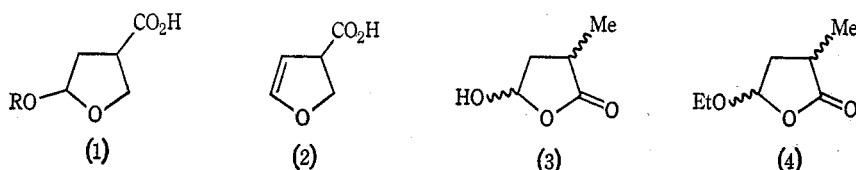
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Abstract

Reduction of 3-furoic acid by lithium in ammonia at -33° proceeds with β -elimination and ring opening and consumption of four equivalents of metal to give (3) and (4). Other products (1) and (2) have been observed from reduction in the presence of a proton source.

Miwa and coworkers¹ have recently reported the reduction of 3-furoic acid under classical Birch conditions (sodium-ammonia-alcohol). The products isolated were acetals of type (1) formed by acid-catalysed addition of alcohol to the reduction product (2) on workup.¹



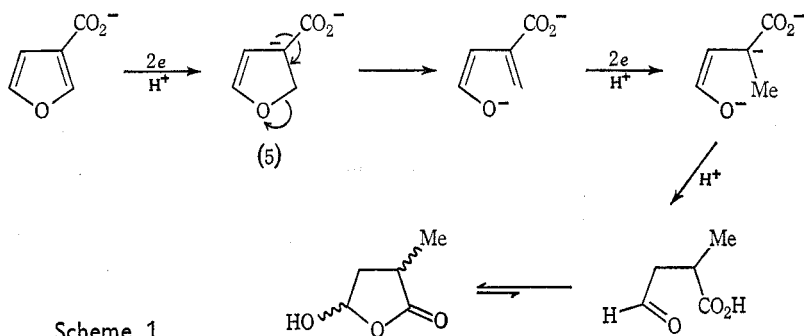
We now find that when no proton source is present, 3-furoic acid consumes four equivalents of lithium at -33° giving, on quenching with ammonium chloride, the hydroxy lactone (3) characterized by its spectral data, as well as its 2,4-dinitrophenylhydrazone derivative.² Ethoxy lactones (4) were also isolated in varying amounts; they result from the workup conditions (continuous extraction into CHCl_3 from the acidified reaction mixture). The ethers (4) showed two g.l.c. peaks in the ratio of 2 : 1 but their separation and purification was precluded by the ready conversion of the pure isomers into an equilibrium mixture. The chemistry of both (3) and (4) has been discussed in some detail.²

The presumed reaction pathway is shown in Scheme 1. As shown by Miwa¹ the reduction takes place as for an isolated α,β -unsaturated acid. We feel the difference in the reaction course lies in the relative rate of protonation of the dianionic intermediate (5) by alcohol as opposed to ammonia (the presumed proton source in our system); the basicity of (5) contrasts to the corresponding dianion from benzoic acid which is

¹ Kinoshita, T., Miyano, K., and Miwa, T., *Bull. Chem. Soc. Jpn*, 1975, **48**, 1865.

² Salmon-Legagneur, F., and Le Goff, Y., *Bull. Soc. Chim. Fr.*, 1965, 1761.

protonated relatively slowly in the presence of methanol.³ There is precedent in the literature for β -elimination of the ether grouping⁴ under our conditions.



Reduction with sodium takes exactly the same course as with lithium and gives the same products in spite of sodium's considerably lower reduction potential in liquid ammonia.⁵ Quenching the reaction with methyl iodide gave little sign of alkylated compounds in the product on workup. Addition of 3-furoic acid to a solution of lithium (2.5 equiv.) in ammonia at -78° (conditions under which a related vinylogous ring opening of 2-furoic acid is suppressed⁶ and under which β -keto enol ethers are reported not to eliminate alkoxide⁷) rapidly consumed the lithium. Immediate quenching with ammonium chloride, however, gave a product which consisted mainly of starting material and (3); only minor peaks for the desired product (2) were visible in the n.m.r. spectrum¹ of the total product.

Experimental

Infrared, nuclear magnetic resonance and mass spectra were measured with a Perkin-Elmer 257 infrared spectrometer, a JEOLCO JNM-MH-100 p.m.r. and an AEI MS902 mass spectrometer. Gas-liquid chromatography was performed on a Varian Aerograph 1700 machine; a 6 ft by 1/4 in. o.d. steel column packed with 5% FFAP on 60/80 Chromosorb W was used.

Reduction Procedure

Small pieces of lithium wire (210 mg, 0.03 g-atom) were added slowly to 3-furoic acid (0.84 g, 0.0075 mol) in liquid ammonia (100 ml) at -33° . The resulting solution slowly turned light yellow, then orange and finally blue (excess of metal) over a period of 20 min. After a further 15 min excess NH_4Cl was added and the NH_3 was removed by evaporation. The residue was dissolved in a minimum of water and acidified carefully at 0° with 4 M HCl . At pH 5 the solution was saturated with solid NaCl and repeatedly extracted into CHCl_3 while the pH was raised to c. 2.5 by further titration with acid. The CHCl_3 layer was washed with a little saturated aq. NaCl solution and removed leaving (3) as a colourless liquid (0.23 g, b.p. $70-75^\circ/0.5$ mm (short path, lit.² $110-112^\circ/4$ mm). ν_{max} (neat) 3400, 1760 cm^{-1} ; p.m.r. spectrum (δ): 1.30 (d, J 7 Hz, 3H, CHCH_3); 1.80–3.05 (m, 3H), 5.3–6.2 (br, 2H); 2,4-dinitrophenylhydrazone, m.p. $179-180^\circ$, from methanol (lit.² 172°); mass spectrum m/e 296 (M^+). Continuous extraction of the combined aqueous

³ Van Bekkum, H., van den Bosch, C. B., van Minnen-Pathuis, G., de Mos, J. C., and van Wijk, A. M., *Recl Trav. Chim. Pays-Bas*, 1971, **90**, 137.

⁴ Shaw, J. E., and Knutson, K. K., *J. Org. Chem.*, 1971, **36**, 1151.

⁵ Harvey, R. G., *Synthesis*, 1970, 161.

⁶ Birch, A. J., and Slobbe, J., *Tetrahedron Lett.*, 1975, 627.

⁷ Watt, D. S., McKenna, J. M., and Spencer, T. A., *J. Org. Chem.*, 1967, **32**, 2674.

fractions with refluxing CHCl_3 over 24 h gave a colourless oil (0.65 g) whose p.m.r. spectrum gave in addition to signals for (3) some further peaks in amounts varying from one reduction to another. G.l.c. analysis (100°) showed 2 peaks (R_t 9.5 and 13 min, ratio 2 : 1); however, preparative g.l.c. of each peak still gave (4) as a 2 : 1 mixture of isomers: ν_{max} 1775 cm^{-1} (lit.² 1775 cm^{-1}); mass spectrum m/e 143 ($\text{M}^+ - 1$, 3.5%), 100 (42), 99 (100), 85 (44), 75 (44), 72 (24), 71 (54), 70 (30), 57 (91).

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Catalysed Gas Phase Decompositions. XXX* Cyclopropane and Boron Tribromide

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Abstract

Boron tribromide in *c.* 10% proportion catalyses the isomerization of cyclopropane at 250–438°C in a homogeneous, molecular reaction. The rate is proportional to the pressures of cyclopropane and boron tribromide and follows the equation

$$k_2 = 10^{9.30} \exp(-68020/8.314T) \text{ s}^{-1} \text{ ml mol}^{-1}$$

Boron tribromide is *c.* 8 times as effective as boron trichloride.

Hitherto the catalysts we have used in the gas phase decompositions of basic organic compounds and in the isomerizations of olefins have been hydrogen halides and carboxylic acids which contain a hydrogen atom that might be made available to the transition state complex.^{1,2} In particular, hydrogen bromide greatly increased the rate of isomerization of cyclopropane,³ reducing the effective temperature from *c.* 500°C to 369–452°C and the activation energy from *c.* 270 to 162 kJ mol⁻¹. Recently, we have shown that boron trichloride, a Lewis acid, is a somewhat more powerful catalyst than hydrogen bromide in this isomerization.⁴ The reaction took place at 360–470° with rate proportional to the pressures of substrate and catalyst and $E = 106.6 \text{ kJ mol}^{-1}$ and $\log A = 11.35$ (A in s⁻¹ ml mol⁻¹). A polar transition state with an internal 1 → 2 shift of a hydrogen atom was proposed.

In solution reactions depending on Lewis acid catalysis, boron tribromide is also effective, and, on the basis of the heats of formation and dipole moments of the pyridine complexes and from the relative catalytic efficiency in alkylation and acylation reactions, it is judged to be a more powerful Lewis acid than boron trichloride.⁵

We now present results for the isomerization of cyclopropane catalysed by boron tribromide.

* Part XXIX, *Aust. J. Chem.*, 1976, 29, 685.

¹ Stimson, V. R., and Tilley, J. W., *Aust. J. Chem.*, 1972, 25, 793.

² Kairaitis, D. A., Stimson, V. R., and Tilley, J. W., *Aust. J. Chem.*, 1973, 26, 761.

³ Ross, R. A., and Stimson, V. R., *J. Chem. Soc.*, 1962, 1602.

⁴ Johnson, R. L., and Stimson, V. R., *Aust. J. Chem.*, 1975, 28, 447.

⁵ Olah, G. A., 'Friedel-Crafts and Related Reactions' Vol. 1, pp. 195, 229, 860 (Interscience: New York).

Experimental

Boron tribromide (B.D.H.) was purified on the line by trap-to-trap distillation. Thirty-eight mixtures in carbon dioxide (2.4–14.5%) were used. The other materials and the general and analytical procedures have been described previously.⁴ The vessel was conditioned regularly with cyclopropane. Control runs for 'zero' time at 352.3°C showed that no significant amount of reaction took place during the manipulative or analytical procedures. Several runs at 315 and 401° taken to 99% completion gave $P_t/P_0 = 0.99 \pm 0.01$. Propene was the only product found. No permanent gas was ever noted when the reaction was pumped out.

Rates

At 311.0°C cyclopropane (119–326 mm) reacted with boron tribromide (15 ± 4 mm) in carbon dioxide to 10.8, 17.5, 33.6, 39.0, 43.0, 50.6, 50.8, 61.2% reaction with $10^5 k_2$ ($s^{-1} \text{ mm}^{-1}$) 4.4, 5.0, 4.9, 4.1, 4.7, 4.0, 4.3, 5.0 (mean 4.6 ± 0.4), respectively. The progress of the reaction therefore follows the first-order form, and propene does not retard or reverse the reaction. Also, as the rate is maintained with *c.* 10% of catalyst, there can be no significant loss of catalyst.

At 299.3° cyclopropane (21.8, 52.2, 81.0, 100.6 mm, variation: 4.6 times) reacted with boron tribromide (6 ± 1 mm) in carbon dioxide with $10^5 k_2$ ($s^{-1} \text{ mm}^{-1}$) 3.6, 3.9, 4.3, 4.2 (mean 4.0 ± 0.4), respectively. Thus the reaction is first order in initial pressure of cyclopropane.

At 272.7° cyclopropane (100 ± 10 mm) reacted with boron tribromide (1.4, 2.5, 3.6, 8.6, 10.5, 10.8 mm, variation: 7.7 times) with $10^5 k_2$ ($s^{-1} \text{ mm}^{-1}$) 1.67, 1.69, 1.60, 1.79, 1.87, 1.88 (mean 1.75 ± 0.1), respectively. Thus the rate is proportional to the pressure of boron tribromide.

Table 1. Variation of rate with temperature

| Temp. (°C) | No. of runs | Cyclopropane (mm) | BBr ₃ (mm) | $10^5 k_2$ ($s^{-1} \text{ mm}^{-1}$) | $10^{-2} k_2$ ($s^{-1} \text{ ml mol}^{-1}$) |
|--------------------|----------------|----------------------|--------------------------|--|---|
| 438.8 | 3 | 138–150 | 8.2–9.3 | 44.1 | 196 |
| 433.7 | 3 | 105–136 | 6.2–13.0 | 45.2 | 199 |
| 425.5 | 3 | 81–122 | 6.9–8.1 | 43.3 | 189 |
| 409.3 | 3 | 162–168 | 8.1–12.1 | 28.1 | 120 |
| 401.0 | 5 | 116–152 | 2.8–13.9 | 24.9 | 105 |
| 381.0 | 4 | 116–140 | 4.6–6.2 | 20.9 | 85 |
| 371.2 | 3 | 131–159 | 4.0–6.2 | 13.6 | 55 |
| 363.2 ^A | 2 | 119–137 | 7.1–9.3 | 14.6 | 58 |
| 362.0 | 4 | 123–152 | 3.5–7.7 | 13.0 | 52 |
| 349.5 | 3 | 132–161 | 4.6–6.7 | 9.4 | 37 |
| 342.5 | 5 | 142–165 | 4.1–9.7 | 7.8 | 30 |
| 330.3 | 3 | 133–154 | 4.5–4.7 | 7.2 | 27 |
| 320.5 | 2 | 134–144 | 4.0–18.0 | 5.54 | 20.5 |
| 311.0 | 9 | 119–326 | 10.4–19.2 | 4.54 | 16.5 |
| 302.7 | 5 | 131–155 | 4.6–13.2 | 3.73 | 13.4 |
| 299.3 | 4 | 21–100 | 5.6–7.0 | 4.01 | 14.3 |
| 296.4 ^A | 2 | 125–167 | 9.7–10.4 | 3.62 | 12.9 |
| 289.5 | 5 | 126–184 | 4.8–6.9 | 2.76 | 9.7 |
| 281.2 | 3 | 138–164 | 7.0–13.4 | 2.49 | 8.6 |
| 272.7 | 6 | 87–114 | 1.4–10.8 | 1.75 | 5.9 |
| 266.1 | 5 | 119–165 | 7.8–11.0 | 1.68 | 5.6 |
| 261.2 | 5 | 97–168 | 4.3–8.2 | 1.21 | 4.0 |
| 258.8 ^A | 4 | 151–164 | 7.5–21.7 | 1.11 | 3.7 |
| 250.0 | 2 | 134–143 | 6.8–8.3 | 1.03 | 3.4 |

^A In packed reaction vessel.

Results and Discussion

Boron tribromide in 2–14% proportion in carbon dioxide catalysed the isomerization of cyclopropane into propene at measurable rate in the temperature range

250–438°C. The progress of the reaction followed the first-order form and was not affected by the propene produced. The second-order rate constants were independent of initial pressures of substrate and catalyst for variations of 4.6 and 7.7 times, respectively. The rates were not affected by an eightfold increase in surface of the reaction vessel. We therefore consider the reaction to be homogeneous and molecular. Apart from random variations the variation of rate with temperature (Table 1) fits well on the straight line appropriate to the Arrhenius equation:

$$k_2 = 10^{9.30 \pm 0.2} \exp(-68020 \pm 2300/8.314T) \text{ s}^{-1} \text{ ml mol}^{-1}$$

The values of A and E are low, particularly in comparison with those found with boron trichloride,⁴ viz. $A = 2.3 \times 10^{11} \text{ s}^{-1} \text{ ml mol}^{-1}$ and $E = 106.6 \text{ kJ mol}^{-1}$. The investigation has been carried out over quite a wide temperature range (189°); however, while the reliability of the rate is satisfactory and the plot showed no curvature, the individual rate constants are not of sufficient accuracy to test modifications of the Arrhenius equation.

Relative rates for catalysed isomerization of cyclopropane are: HBr, 1; BCl₃, 16; BBr₃, 140. Boron tribromide is a more effective catalyst than boron trichloride⁴ by a factor of 8.8 times, as measured by the relative rates at 400°C, and this is consistent with the polar mechanism suggested.

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