

THE OXIDATIVE REARRANGEMENT OF KETONES TO CARBOXYLIC ACIDS

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THE interaction of hydrogen peroxide and selenium dioxide with olefins yields 1,2-¹ and 1,3-² glycols. Use of these reagents with cyclic ketones³ gives cycloalkanecarboxylic acids by oxidative ring contraction.

We now wish to report that open-chain ketones also rearrange. Details of the treatment of acetone and phenylacetone are given below. Acetone was converted to propionic acid (39%), identified as the ethyl ester. Phenylacetone rearranged predominantly to hydratropic acid (11%) and to a slight extent to hydrocinnamic acid (0.6%), identified as the methyl esters.

We have also found that substitution of selenic acid and pyridine for selenium dioxide gives superior yields of ring contraction products. For example, cyclohexanone and excess hydrogen peroxide with approximately 3 mol % selenic acid and 10 mol % pyridine produced 64% cyclopentane-carboxylic acid. Competition by ring enlargement (Baeyer-Villiger), previously undetected,³ was evidenced by the isolation of 10-30% ethyl 6-hydroxycaproate.

We are continuing our study of the scope and mechanism of this reaction.

¹ P. Seguin and M. Delepine, C. R. Acad. Sci., Paris **216**, 667 (1943);
M. Mugdan and D. P. Young, J. Chem. Soc. 2988 (1949).

² A. Stoll, A. Lindenmann and E. Jucker, Helv. Chim. Acta **36**, 268 (1953).

³ G. B. Payne and C. W. Smith, J. Org. Chem. **22**, 1680 (1957).

ExperimentalOxidation of acetone

A solution of acetone (29 g, 0.5 mole), t-butyl alcohol (150 ml), 30% hydrogen peroxide (100 ml, 1 mole) and selenic acid (sp. gr. 1.4, 4 ml) was refluxed for 6 hr, made strongly alkaline with 40% potassium hydroxide solution, refluxed for an additional hour, and t-butyl alcohol was removed by steam distillation. The acids were isolated by acidification, steam distillation, salting-out, and ether extraction. Distillation of the ethyl esters gave A, b.p. 75-80°, 19 g; B, b.p. 80-99°, 8 g; residue, 2 g. Distillation of the residue gave C, b.p. 98-99°, 1 g. Gas chromatography of the distillates showed an over-all composition of 20% ethanol, 9.6% ethyl acetate and 71% ethyl propionate (39% based upon acetone), and about 0.1% of unidentified material. Fraction C, which was 96% ethyl propionate, formed a p-toluide,⁴ m.p. 125-6° (lit.⁵ m.p. 126°), undepressed when mixed with an authentic sample.

Oxidation of phenylacetone

A two-phase mixture of phenylacetone (34 g, 0.25 mole), t-butyl alcohol (150 ml), 30% hydrogen peroxide (50 ml, 0.5 mole), selenic acid (sp.gr. 1.4, 4 ml) and pyridine (4 ml) was refluxed for 21 hr, treated with 100 ml of 30% potassium carbonate solution, and extracted with ether. The acids were isolated by acidifying the aqueous solution and extracting with chloroform. Vacuum distillation of the methyl esters gave 5 g of product, shown by gas chromatography to consist of 87% methyl hydratropate (11% based upon phenyl-

⁴ S. S. Jenkins, J. Amer. Chem. Soc., 55, 3049 (1933).

⁵ C. A. Bischoff, Liebigs Ann., 279, 172 (1894).

acetone), 5.1% methyl hydrocinnamate (0.6% based upon phenylacetone), 6.6% methyl benzoate and 1.3% methyl phenylacetate. Treatment with benzylamine⁶ gave a benzylamide, m.p. 78.5-9.5°, which showed no depression when mixed with an authentic sample prepared from hydratropic acid (Found: C, 80.84; H, 7.14; N, 6.01. $C_{16}H_{17}NO$ requires C, 80.32; H, 7.16; N, 5.86%).

⁶ O. C. Dermer and J. King, J. Org. Chem. **8**, 168 (1943).