

REDUCTION OF FLUORENONE-4-CARBOXYLIC ACID, ITS ACID CHLORIDE AND METHYL ESTER

ROBERT L. SUBLETT, HOWARD G. ASHBURN, AND JIMMY GALE RICHARDSON

Tennessee Technological University, Cookeville, Tennessee

INTRODUCTION

The only reduction of fluorenone-4-carboxylic acid or its derivatives cited in literature is the reduction of the keto carbonyl group with zinc and ammonium hydroxide (2). Fluorenone-4-carboxylic acid, or its derivatives, contains two reducible groups: the keto carbonyl and the acid carbonyl group. Therefore, by the selection of the reducing agent and the conditions, three different combinations of group reductions should be possible: the reduction of both carbonyl groups, the reduction only of the keto carbonyl, or the reduction only of the acid carbonyl group.

Brown and Rao (1) cite an unpublished communication from Dr. K. Ichikawa that sodium borohydride in diglyme solution reduces the acid chloride group more readily than the ketone or the aldehyde group. Lithium aluminum hydride reduces both the acid and keto carbonyl groups. Sodium borohydride, a milder reducing agent, is almost specific for ketone and aldehyde groups.

The study below is an attempt to accomplish these selective reductions of keto carbonyl groups and acid carbonyl groups of fluorenone-4-carboxylic acid, or its derivatives, using sodium borohydride and lithium aluminum hydride.

EXPERIMENTAL

(a) *Reductions Using Lithium Aluminum Hydride.* 9-Hydroxyfluorene-4-carboxylic acid, methyl fluorenone-4-carboxylate, and fluorenone-4-carboxylic acid chloride were reduced with lithium aluminum hydride to yield in all cases the 9-hydroxy-4-(hydroxymethyl) fluorene. The alcohol was identified by carbon and hydrogen analysis, infrared spectra, and the preparation of the diacetate derivative (melting point, 108-109° C).

A typical preparation is as follows: Four grams (0.10 mole) of lithium aluminum hydride was placed in 200 milliliters of anhydrous ether and the mixture was refluxed with constant stirring for thirty minutes. A suspension of four grams (0.018 mole) of fluorenone-4-carboxylic acid in 300 milliliters of anhydrous ether was added to the reducing solution as fast as refluxing permitted. After the mixture was allowed to reflux for twenty hours, water was added to react with any excess lithium aluminum hydride and then dilute sulfuric acid to decompose any metal complexes. The remaining solid inorganic materials were removed by filtration. The ether layer was separated and evaporated to dryness leaving a yellow residue, which was washed with a 5 per cent sodium bicarbonate solution in order to remove any unreduced acid. Further purification was accom-

plished by suspension, in ether, filtering, dissolving in 95 per cent ethanol, and boiling with Norit A. White crystals, melting at 210-211° C, were obtained in 50 per cent of theoretical yield. The infrared spectrum showed the presence of hydroxyl groups and no carbonyl or carboxyl groups. From this and the analysis it was concluded that the product was 9-hydroxy-4-(hydroxymethyl) fluorene. Analysis, calculated for $C_{14}H_{12}O_2$ found C, 79.31%; H, 5.71% and C, 78.82%; H, 6.09%. The calculated molecular weight for $C_{14}H_{12}O_2$ was 212, the molecular weight (Rast) was 207. The same product was obtained when the temperature and time of reaction were changed. Results are given in Table I.

(b) *Reductions Using Sodium Borohydride.* The selective reduction of the acid carbonyl group in preference to the keto was attempted on: (a) fluorenone-4-carboxylic acid, (b) fluorenone-4-carboxylic acid chloride, and (c) methyl fluorenone-4-carboxylate under various conditions. The conditions varied were temperature, molar ratio of reducing agent to compound, and addition of aluminum chloride. Sodium borohydride alone would not reduce either group, but when mixed with aluminum chloride, it reduced either the keto carbonyl only, or both groups. The results are given in Table I.

The following is a typical reduction using sodium borohydride and aluminum chloride: Two-tenths gram (0.005 mole) of sodium borohydride was placed in fifty milliliters of diglyme and stirred for fifteen minutes. Two grams (0.008 mole) of fluorenone-4-carboxylic acid chloride and two-tenths gram (0.0015 mole) of aluminum chloride dissolved in a minimum amount of diglyme were added in that order. The reaction mixture became hot and was allowed to cool, after which it was heated to 100° C for one hour to complete the reaction. The solution was poured into a beaker containing 100 grams of cracked ice and thirty milliliters of concentrated hydrochloric acid to decompose any metal complexes. The yellow precipitate was filtered, washed three times with 100 milliliter portions of 5 per cent sodium bicarbonate solution, dissolved in 95 per cent ethanol, and boiled with Norit A. White crystals, melting at 203-204° C, were obtained in a yield of 75 per cent of theoretical.

DISCUSSION

From the results obtained in this study, lithium aluminum hydride gave no indications of selectivity toward the keto or carboxyl group and reduced both groups in each reduction attempted. Sodium boro-

Table 1
Products and reduction conditions of fluorenone-4-carboxylic acid and derivatives.

Oxidant	Reductant	Reductant Oxidant	Product	% Yield	Melting Point
Fluorenone-4-carboxylic acid	LiAlH ₄ ¹	5:1	9-hydroxy-4-(hydroxy methyl) fluorene	50	210-211
	NaBH ₄	1:1.5	9-hydroxy-fluorene-4-carboxylic acid	51	203-204
Methyl fluorenone-4-carboxylate	LiAlH ₄	5:1	9-hydroxy-4-(hydroxy methyl) fluorene	76	210-211
	NaBH ₄	1:1.5	methyl fluorenone-4-carboxylate	94	138-139
	NaBH ₄	3:1	9-hydroxy-4-(hydroxy methyl) fluorene	79	210-211
Fluorenone-4-carboxylic acid chloride	LiAlH ₄ ²	5:1	9-hydroxy-4-(hydroxy methyl) fluorene	79	210-211
	NaBH ₄	1:1.6	9-hydroxy-4-carboxylic acid	63	203-204
	NaBH ₄ ³	3:1	9-hydroxy-4-(hydroxy methyl) fluorene	94	210-211

¹ At 0°, 40% yield of the same product

² AlCl₃ gave poor yield of the same product

³ No AlCl₃, no reduction

hydride, however, could be used in the reduction of only the keto or in the reduction of both carbonyl groups. Under the experimental conditions used in this study, sodium borohydride in diglyme solution failed to reduce the acid chloride group more readily than the keto. This result was in disagreement with the information given by H. C. Brown and B. C. S. Rao from the un-

published works of Dr. K. Ichikawa; however, sodium borohydride did exhibit a selectivity for the keto carbonyl over the acid carbonyl in all cases.

LITERATURE CITED

- Brown, H. C. and Rao, B. C. S. 1956. *J. of Am. Chem. Soc.*, 78:2582.
Graebe, C. and Aubin, C. 1888. *Ann.*, 247, 284.

NEWS OF TENNESSEE SCIENCE

(Continued from page 34)

Society and the American Society for Engineering Education. The conferences are designed primarily for university and college faculty members. Further information can be obtained from: Special Projects Office, Oak Ridge Associated Universities, P. O. Box 117, Oak Ridge, Tennessee 37831.

The 16th Annual Wildflower Pilgrimage sponsored in part by the Department of Botany, The University of Tennessee, will be held at Gatlinburg, Tennessee, in the Great Smoky Mountains National Park April 28-30, 1966. For further details write to the Department of Botany, University of Tennessee, Knoxville, Tennessee 37916.

The Twenty-Fourth Annual Meeting of the Tennessee Junior Academy of Science will be held at Vanderbilt University, April 15 and 16, 1966. Dr. Wendell G. Holladay, Chairman of the Department of Physics and Astronomy, will serve as local chairman.

All Tennessee High Schools are urged to participate in the TJAS programs leading up to the Spring meeting. This program provides state-wide and national recognition for high school students' investigative—or research-type science projects.

(Continued on page 48)