moistened with caustic solution, the imprint gives an intense blue fluorescence in ultraviolet light, but shows no yellow-green fluorescence due to the photoeffect. It appears therefore that coumarin occurs only in the interior of the bean, while the outer skin contains only hydroxycoumarin.

Organic Reductions by Sodium Aluminum Hydride

By A. E. Finholt, E. C. Jacobson, A. E. Ogard and P. Thompson

Received March 2, 1955

The development of new procedures for preparing sodium aluminum hydride[1] made possible a preliminary study of the scope of organic reductions with this hydride. If one assumes that reductions take place through a mechanism involving a negative ion such as AlH_4^-,[2] there should be little difference in the action of sodium aluminum hydride as compared with lithium aluminum hydride. The data in Table I indicate that reductions are similar for the two hydrides with aldehydes, ketones, carboxylic acids, esters, acid chlorides, alkyl halides, nitriles and the aryl and aliphatic nitro compounds. The yields in each example in Table I except for butanone-2 are within 10% of those reported for the reduction of the same compound with lithium aluminum hydride. The products were isolated and identified in the usual standard way.

Table I

Reductions by Sodium Aluminum Hydride

Compound reduced	Product	Yield, %
n-Heptaldehyde	*n*-Heptyl alcohol	79
Butanone-2	*s*-Butyl alcohol	64
Benzoic acid	Benzyl alcohol	81
Ethyl benzoate	Benzyl alcohol	91
Palmityl chloride	Cetyl alcohol	96
Acetanilide	N-Ethylaniline	63
1-Iodohexadecane	Hexadecane	85
Nitrobenzene	Azobenzene	78
Nitrobutane	1-Aminobutane	73
Cinnamaldehyde	Hydrocinnamyl alcohol	89
Cinnamaldehyde	Cinnamyl alcohol	85[a]
Benzonitrile	Benzylamine	92
Benzonitrile	Benzaldehyde	70[a]

[a] Inverse addition of the hydride to the organic compound. The benzaldehyde preparation was run at 0° and the cinnamyl alcohol preparation at room temperature.

The reductions of cinnamaldehyde and benzonitrile were undertaken to see if cinnamyl alcohol and benzaldehyde could be prepared by the normal reduction procedure in which the organic compound is added to the hydride. This was the procedure for all the reductions listed in Table I except those indicated by note *a*. As with lithium aluminum hydride,[3] it turned out that the unsaturated alcohol and the aldehyde could be obtained only by the inverse addition of sodium aluminum hydride to the organic compound. Thus sodium aluminum hydride was no milder a reagent than lithium aluminum hydride.

All the reactions were given ample time to be completed. These studies, therefore, do not rule out the possibility that the rates of reduction of sodium and lithium aluminum hydride may be different. There is little doubt, however, that sodium aluminum hydride can be substituted effectively for lithium aluminum hydride in most organic reductions.

Experimental

The same general experimental conditions were employed as those described for lithium aluminum hydride[4] except that diethyl ether could not be used as a solvent. All of the reductions except that of butanone-2 were run using a tetrahydrofuran solution of sodium aluminum hydride. With the ketone, the solvent was the dimethyl ether of triethylene glycol. One run (not reported in Table I) was made using a slurry of sodium aluminum hydride in diethyl ether. An 82% yield of benzyl alcohol was obtained by adding ethyl benzoate to the slurry.

General Procedure.—A stock solution of sodium aluminum hydride in tetrahydrofuran was prepared from aluminum hydride and sodium hydride.[1] The solution was standardized in the usual way by removing the solvent from an aliquot and hydrolyzing the solid; the strength of the solution was about 3% by weight. Commercial tetrahydrofuran was purified for all purposes by distillation from lithium aluminum hydride, taking care not to distil to dryness. The compound to be reduced usually was diluted with tetrahydrofuran. The tetrahydrofuran solution of sodium aluminum hydride was weighed into the reaction vessel; the system was swept with dry nitrogen gas, and the compound to be reduced was added dropwise to the sodium aluminum hydride solution. Stirring was maintained throughout the addition, the reaction period, and the decomposition of the excess hydrate with water. The reactions proceeded very smoothly and without undue liberation of heat. Periods allowed for the reaction varied from 2 to 17 hours. The excess sodium aluminum hydride was decomposed by addition of water; the intermediate complex was broken up by addition of either 10% sulfuric acid or 10% sodium hydroxide, sometimes with heating. One example will be given to illustrate the general procedure.

The Reduction of Ethyl Benzoate.—A solution of 25 g. (0.166 mole) of ethyl benzoate dissolved in 25 g. of tetrahydrofuran was added slowly to 250 g. of tetrahydrofuran containing 6.0 g. (0.111 mole) of sodium aluminum hydride. The mixture was stirred for 2.5 hours. After decomposition of excess hydride with water, 10% sodium hydroxide solution was added to break up the complex. The product was extracted from the reaction vessel with diethyl ether; this solution was dried over calcium sulfate, filtered, and distilled to remove ether and tetrahydrofuran. The product was fractionally distilled to give 16.4 g. (91%) of benzyl alcohol, b.p. 205–207°.

Acknowledgment.—The authors wish to thank the Office of Naval Research for financial support in this investigation.

Department of Chemistry
St. Olaf College
Northfield, Minnesota

---

[1] To be published by A. E. Finholt, G. D. Barbaras, G. K. Barbaras, G. Urry, T. Wartik and H. I. Schlesinger.

[2] L. W. Trevoy and W. G. Brown, This Journal, **71**, 1675 (1949).

[3] F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

[4] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley & Sons, Inc., New York, N. Y., 1951, Chapter 10.

Thiophenetricarboxylic Acids

By Reuben G. Jones

Received March 19, 1955

Recent communications[1,2] have described the preparation of 3,4-thiophenedicarboxylic acid. With the addition of this member to the series, all the mono- and dicarboxylic acids of thiophene and thiophenetetracarboxylic acid are known. The two tricarboxylic acids, 2,3,4-thiophenetricarboxylic

---

[1] J. Sice, *J. Org. Chem.*, **19**, 70 (1954).

[2] E. C. Kornfeld and R. G. Jones, *ibid.*, **19**, 1671 (1954).