mixed anhydrides were relatively pure and were not mixtures of two distinctly different anhydrides. While a combustion analysis could not be conclusive, it is interesting to note that such results, as well as molecular refractions, substantiated the same conclusions. The mixed anhydrides, besides having considerable theoretical significance, are useful in the Friedel–Crafts reaction, for the preparation of mixed esters of polyhydroxy compounds, and by disproportionation for the synthesis of high molecular weight simple anhydrides, together with acetic anhydride as a by-product.

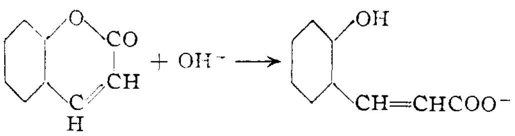
SCHOOL OF CHEMICAL TECHNOLOGY
NORTH DAKOTA STATE COLLEGE
FARGO, NORTH DAKOTA

A Sensitive and Specific Test for Coumarin through Photocatalysis[1]

BY F. FEIGL, H. E. FEIGL[2a] AND D. GOLDSTEIN[2b]

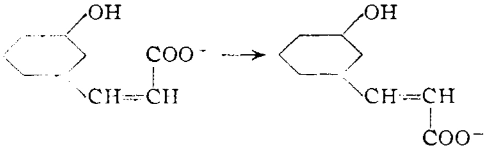
RECEIVED MARCH 11, 1955

When coumarin is dissolved in dilute alkali, the pyrone ring opens with production of the alkali salt of *o*-hydroxycinnamic acid. We have found



that freshly prepared alkaline solutions show no fluorescence at first if observed under a quartz lamp, but continued exposure produces gradually a yellow-green fluorescence, whose intensity increases to a maximum. This effect can be strikingly demonstrated. A small quantity of coumarin is dissolved in 1 *N* alkali and a drop of the solution is placed on filter paper. After one or two minutes of irradiation, the fleck begins to fluoresce yellow-green. Alternatively, a part of the fleck may be covered with a coin or black paper and then exposed, for 3–8 minutes, to the action of the ultraviolet rays. When the shielded area is uncovered, a crescent-shaped zone or segment of a circle displaying intense yellow-green fluorescence stands out sharply from the non-fluorescing area. If the irradiation is then continued, the part of the fleck originally covered begins to fluoresce and after sufficient exposure the entire surface of the fleck displays a uniform fluorescence intensity

If a freshly prepared solution of coumarin in alkali is protected from the light, no fluorescence is observed even after several months. In contrast, alkaline solutions exposed to diffused daylight show a faint but distinct fluorescence even within 10–12 hours. Accordingly, the fluorescence of an alkaline solution of coumarin is initiated by irradiation and it seems that the action of the ultraviolet accelerates the change of a non-fluorescing into a fluorescing compound, a change that normally proceeds at an immeasurably small rate. It seems logical to suppose that when coumarin is dissolved in alkali, the initial product is the non-fluorescing *cis* form I of *o*-hydroxycinnamic acid, which is rearranged by the ultraviolet irradiation into the fluorescing isomeric *trans* form II



I II

Our trials thus far show that the light effect observed with coumarin also occurs with alkaline solutions of those coumarin derivatives which have no free OH groups in the benzene ring. Substituents appear to have an influence on the speed with which the fluorescence becomes visible. For example, when a drop of an alcohol basic solution of bergapten is placed on filter paper and subjected to ultraviolet irradiation, the fluorescence does not appear until after about 10 minutes' exposure, and furthermore the intensity of the fluorescence increases much more slowly than with a coumarin solution of the same molarity.

Coumarin derivatives, such as umbelliferone, esculetin, daphnetin, etc., which have free OH groups in the benzene ring, fluoresce deep blue in the solid state and in basic solution. No photo effect could be found in alkaline solutions of these compounds.

The fluorescence after irradiation with ultraviolet light of drops of alkaline solutions of coumarin placed on filter paper will reveal the presence of as little as 0.005 γ of coumarin. This corresponds to a dilution limit of 1:10,000,000. However, this type of test is not reliable for detecting coumarin because alkaline solutions of its derivatives without OH groups show the same behavior and because the self-fluorescence of hydroxycoumarins makes it difficult to see the yellow-green-fluorescence produced by the irradiation with ultraviolet light. (Within certain concentration limits, it appears possible to detect compounds, which fluoresce blue or yellow-green, by capillary (absorptive) separation on filter paper. This points to a possible employment of the coumarin test in paper chromatography.)

A specific test for coumarin can be achieved if advantage is taken of the fact that only coumarin has an appreciable vapor tension at room temperature or when gently warmed. Consequently, it is possible to allow the coumarin vapor to come into contact with a solution of alkali to yield compound I which can then be irradiated to produce the isomeric fluorescing compound II. The procedure in this case is: A drop of the ether test solution is evaporated in a micro test-tube or a tiny sample of the solid is taken. The open end of the tube is covered with a piece of filter paper moistened with alkali solution and the bottom of the tube is plunged into hot water. After several minutes, the paper is held under a quartz lamp. If coumarin is present, a yellow-green fluorescence appears in a short time. Leaves and other plant parts can be tested for coumarin by this simple method.

The following experiment is worth noting. A bean of *Torresia cearensis* (coumarin content about 0.3%) is cut in two with a sharp knife and the face of the section is pressed for several seconds against filter paper moistened with alkali. If the paper is then exposed under the quartz lamp, the impression begins to fluoresce intensively after 1–2 minutes. If the imprint is previously half covered with black paper, the photoeffect (lack of fluorescence of the covered portion) is very striking. If an uncut bean is pressed against paper

---

(1) Translated from the German manuscript, by Ralph E. Oesper, University of Cincinnati.

(2) (a) Deceased. (b) Laboratorio da Produçao Mineral, Ministerio da Agricultura, Rio de Janeiro, Brazil.

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).