dilutions necessary to cover the entire spectrum (one dilution for each log ϵ unit). The spectra in each of the two hydroxylated solvents showed appreciable deviations from Beer's law and uniformly much lower absorption than in isoöctane. Only the curves in water and in isoöctane are shown in Fig. 2; the curve in alcohol was similar in form to, and intermediate in intensity between, the spectra in water and isoöctane.

As a model compound to demonstrate the magnitude of contributions from hydrated forms, the tetraacetate of *o*-phthalaldehyde was prepared according to the directions of Thiele and Winter.[20] As anticipated, its spectrum had the appearance characteristic of benzene, toluene, xylenes, etc., and its intensity of absorption was much weaker than that of the aldehyde. In dilute aqueous hydrochloric acid its solutions readily hydrolyzed, whereupon the spectra of the resulting solutions assumed the appearance of aqueous solutions of *o*-phthalaldehyde.[21]

Ninhydrin (Triketohydrindene Hydrate).—Commercial ninhydrin (Paragon Testing Laboratories) was recrystallized from water giving almost colorless needles. The spectrum in water is very similar to that of *o*-phthalaldehyde in isoöctane, except for the peak in the far ultraviolet region, which occurs nearer the visible with ninhydrin than with the aldehyde.

Attempts to Resolve Compound II.—Since the structure proposed for the active antihemorrhagic salt contains one asymmetric carbon atom, it should exist in enantiomorphic forms and should form two diastereoisomeric salts with an optically active cation. Several attempts were made to prove the existence of such stereoisomerism by formation of crystalline salts with *l*(+)-arginine hydrochloride[22] and with quinine methiodide. These salts did not appear to be suitable for resolution, and no conclusive results were obtained.

Summary

1. On the basis of spectrometric comparison with several simple *o*-benzenedicarbonyl compounds, the actively antihemorrhagic sodium bisulfite addition product of 2-methyl-1,4-naphthoquinone is assigned the structure sodium 2-methyl-1,4-dioxotetralin-2-sulfonate.

2. The formation of the active salt, "Menadione Sodium Bisulfite," its reconversion into Menadione under certain conditions, and other properties are accounted for on the basis of reasonable reactions.

3. *o*-Phthalaldehyde exists largely in solvated forms in water and alcohol solutions.

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[20] Thiele and Winter, *Ann.*, **311**, 360 (1900).

[21] The spectra of *o*-phthalaldehyde in various solvents have been reported previously: (a) Valyashko and Boltina, *J. Russ. Phys. Chem. Soc.*, **46**, 1741 (1914), *C. A.*, **9**, 2070 (1915); (b) Purvis, *J. Chem. Soc.*, **105**, 2482 (1914). Since it is difficult to translate these older data into modern terminology, it seemed desirable to repeat the spectrometric measurements under conditions comparable with those used for the naphthoquinone derivatives.

[22] Harris, Mozingo, Wolf, Wilson and Folkers, THIS JOURNAL, **67**, 2100 (1945).

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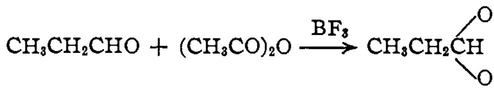
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

Boron Fluoride Catalyzed Addition of Aliphatic Anhydrides to Aldehydes[1]

BY EUGENE H. MAN, JAMES J. SANDERSON[2] AND CHARLES R. HAUSER

In an attempt to acetylate propionaldehyde with acetic anhydride by the boron fluoride method for the acetylation of ketones to form β-diketones,[3] we were unable to isolate any of the expected β-ketoaldehyde. Instead, there was obtained propylidene diacetate which was formed presumably by the addition of the anhydride to the carbonyl group of the aldehyde in accordance with the equation



$$CH_3CH_2CHO + (CH_3CO)_2O \xrightarrow{BF_3} CH_3CH_2CH(OCOCH_3)_2$$

Whereas the acylation of ketones with anhydrides requires an equivalent amount of boron fluoride,[3] the addition of acetic anhydride to the carbonyl group of the aldehyde requires only a catalytic amount of this reagent.

The addition reaction has been realized with various aldehydes and anhydrides. The results are summarized in Table I. On the basis of preliminary experiments, the procedure (Method A) adopted in the reactions with acetic anhydride consists in adding the aldehyde to excess of the anhydride accompanied by the addition, from time to time, of a few drops of boron fluoride etherate.[4] In no case were there more than twenty drops of the etherate required in order to produce the maximum yield, although the yield appeared not to be lowered by the presence of slightly more than an equivalent amount of the catalyst. This method, employing only a catalytic amount of boron fluoride, was found most satisfactory also with *n*-butyric anhydride and benzaldehyde, but it produced mixtures of products with *n*-butyric or propionic anhydride and other aldehydes. The procedure (Method B) adopted in these other cases consists in adding a mixture of the anhydride and aldehyde to 10% more than an equivalent of the boron fluoride etherate catalyst. Both Methods A and B gave mixtures of products with acetic anhydride and formaldehyde. The reaction appeared to fail with succinic anhydride and propionaldehyde.

Wegscheider and Späth[5] have effected the addi-

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[1] Part of this work was carried out under Contract N7onr-455 with the Office of Naval Research.

[2] Carbide and Carbon Chemicals Corporation Fellow, 1946–1948.

[3] See Hauser and Adams, THIS JOURNAL, **66**, 345 (1944); Adams and Hauser, *ibid.*, **67**, 284 (1945).

[4] Eastman Kodak Co. reagent containing 45% by weight of boron fluoride was employed.

[5] Wegscheider and Späth, *Monatsh.*, **30**, 825–869 (1909); see also Kirrmann, *Bull. soc. chim.*, **53**, 295 (1933).

TABLE I[a]

YIELDS OF ADDITION PRODUCTS FROM ALDEHYDES AND ANHYDRIDES IN THE PRESENCE OF BORON FLUORIDE

Aldehyde	Anhydride	Method	Product	B. p. °C.	Mm.	Yield, %
Acetaldehyde	Acetic	A	Ethylidene diacetate	54–55	10	65
Propionaldehyde	Acetic	A	Propylidene diacetate	68.5–70	12	73
Isobutyraldehyde	Acetic	A	Isobutylidene diacetate	74–76	10	80
Benzaldehyde	Acetic	A	Benzylidene diacetate	134.5[b]	10	80[c]
Propionaldehyde	Propionic	B	Propylidene dipropionate[d]	110–111	10	73
Propionaldehyde	Butyric	B	Propylidene dibutyrate[e]	88–88.5	10	71.5
Benzaldehyde	Butyric	A	Benzylidene dibutyrate[f]	160–162	3.5	81

[a] Analyses are by Clark Microanalytical Laboratory, Urbana, Illinois. [b] M. p. 43.5–44°. [c] The yield of crude product, m. p. 41–43°, was 87%. [d] *Anal.* Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.54; H, 8.35. [e] *Anal.* Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 61.34; H, 8.96. [f] *Anal.* Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.39; H, 7.56.

tion of acetic and other anhydrides to various aldehydes in the presence of catalytic amounts of sulfuric acid or certain other H-acids. However, with the possible exception of the reaction producing benzylidene diacetate, their yields were considerably lower than those given in Table I. Moreover, they usually employed longer reaction times.

In an attempt to effect the acyloin reaction with benzylidene dibutyrate according to a procedure employed with methyl *n*-butyrate,[6] we obtained a solid, melting at 99–104° after five recrystallizations from ethanol, which evidently was not butyroin. The product was not identified.

Experimental

Method A.—A 500-ml. round-bottomed, three-necked flask having ground-glass joints was equipped with a mercury-sealed stirrer, a dropping funnel fitted with a drying tube, and an attachment containing a thermometer and an air outlet protected with a drying tube. In the flask, immersed in a salt-ice slush, was placed 0.75 mole of acetic anhydride and the stirrer started. Maintaining the temperature at 0–5°, five drops of boron fluoride etherate[4] was added, followed by 0.5 mole of the aldehyde added dropwise over a period of two and one-half hours. An additional two or three drops of the boron fluoride etherate was added each half-hour during the addition of the aldehyde. After stirring the reaction mixture for another hour, 400 ml. of a 10% sodium acetate solution was added, and the resulting mixture stirred rapidly for twenty minutes. The oily layer was extracted with two 100-ml. portions of ether, and the ethereal extracts washed twice with 100-ml. portions of a saturated sodium bicarbonate solution, and twice with 100-ml. portions of distilled water. The washed ether solution was dried over Drierite, the ether distilled, and the product fractionated *in vacuo* in a 100-ml. Spitz flask fitted with a 15-cm. Vigreux column.

Method B.—In a one-liter round-bottomed three-necked flask, equipped as described above, was placed 150 ml. (about 1.1 moles) of boron fluoride etherate. Maintaining the temperature at 0–5°, a mixture of 0.75 mole of the anhydride and 0.5 mole of the aldehyde was added dropwise over a period of an hour with rapid stirring. After stirring the reaction mixture for two hours longer, 500 ml. of a 10% sodium acetate solution was added and the resulting mixture stirred rapidly for forty-five minutes. The oily layer was extracted with two 100-ml. portions of ether, and the ethereal extracts washed with 100-ml. portions of saturated sodium bicarbonate solution until no further evolution of carbon dioxide took place on shaking the ether solution with a fresh 100-ml. portion of the bicarbonate solution. The ether solution was then washed with two 100-ml. portions of distilled water, and dried over Drierite. The ether was distilled, and the product fractionated *in vacuo* in a 100-ml. Spitz flask fitted with a 15-cm. Vigreux column.

Summary

1. Boron fluoride has been found to catalyze the addition of aliphatic anhydrides to the carbonyl group of aliphatic and aromatic aldehydes to form diesters.

2. In general, the yields have been better with this reagent than with sulfuric acid or phosphoric acid.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 1, 1949

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(6) Hansley, THIS JOURNAL, 57, 2303 (1935).