TABLE I

ACYL DERIVATIVES OF *o*-ANISIDINE

Acyl groups	Solvent used in crystn.	Yield, %	M. p., °C.	Formula	Nitrogen % Calcd.	Nitrogen % Found
Propionyl	Ether[a]	73	33.5-34.5	$C_{10}H_{13}NO_2$	7.82	7.80
Butyryl	Ether[a]	78	24.5-25.5	$C_{11}H_{15}NO_2$	7.25	7.11
Valeryl	Ether[a]	91	25.5-26.5	$C_{12}H_{17}NO_2$	6.76	6.45
Isovaleryl	Ether[a]	94	49-49.5	$C_{12}H_{17}NO_2$	6.76	6.59
Caproyl	Ether[a]	61	33-33.5	$C_{13}H_{19}NO_2$	6.33	6.38
Heptanoyl	Pet. ether	67	42-43	$C_{14}H_{21}NO_2$	5.96	5.73
Phenylacetyl[b]	Dilute alc.	88	82.5-83			
Hydrocinnamyl	Isopropyl ether or benzene and heptane	100	59.5-60	$C_{16}H_{17}NO_2$	5.49	5.50
m-Bromobenzoyl		86	112.5-113	$C_{14}H_{12}BrNO_2$	4.58	4.59
					Br, 26.11	25.60
p-Anisoyl		100	96.5-97.5	$C_{15}H_{15}NO_3$	5.45	5.42
Benzoyl[c]			66-67			
Acetyl[d]			85-85.5			
Dibenzoyl	Alc. or toluene	60	149.5-150	$C_{21}H_{17}NO_3$	4.23	4.25
Dipropionyl	Hexane	85	62.5-63.5	$C_{13}H_{17}NO_3$	5.96	5.98

[a] By cooling with solid carbon dioxide.

[b] Aggarwal, Das and Rây[2] prepared this compound from *o*-anisidine and phenylacetic acid and reported a melting point of 84°.

[c] Prepared by Mühlhäuser,[1] who reported a melting point of 59.5°.

[d] Mühlhäuser[1] reported a melting point of 78°. Our melting point agrees with the one given in Mulliken's "Identification of Pure Organic Compounds," Vol. II, p. 151.

soluble in ether, and almost insoluble in hexane. *o*-Dibenzoylanisidine is difficultly soluble in toluene and alcohol but readily soluble in chloroform. *o*-Dipropionylanisidine is soluble in practically all organic solvents.

One additional compound was prepared during this investigation. Its properties are given below.

o-Benzoylmethylaminophenyl Benzoate.—This compound was prepared by the Schotten-Baumann method in 40% yield. It was crystallized from alcohol. It is soluble in dioxane, acetone, chloroform and benzene; somewhat soluble in alcohol and ether; and almost insoluble in petroleum solvents, m. p. 114-115°.

Anal. Calcd. for $C_{21}H_{17}NO_3$: N, 4.25. Found: N, 4.12.

(2) Aggarwal, Das and Rây, *J. Ind. Chem. Soc.*, **6**, 717 (1929).

DEPARTMENT OF CHEMISTRY
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Addition of Methyl Alcohol to Dialkylacetylenes

BY G. F. HENNION AND J. A. NIEUWLAND

The many well-known reactions of acetylene and its homologs with hydroxylated compounds (alcohols, carboxylic acids, etc.) are characterized by the fact that they proceed quite readily in an appropriate acid medium in the presence of a small amount of a suitable mercuric salt. The mechanism of this catalysis has engaged our attention for some time. There is little doubt but what the reaction of an acetylene with methyl alcohol, for example, produces first a vinyl ether which in turn immediately adds a second molecule of alcohol to form the ketal or acetal. There is evidence to indicate that the mercuric salts function only in the first of these reactions.

In attempting to determine whether the catalytic mercuric salt forms an intermediate with the acetylene by addition or substitution (or both) we have succeeded in adding methyl alcohol to two dialkylacetylenes in the usual way.[1] This indicates quite clearly that an intermediate of the mercury acetylide type is not essential to the mechanism of catalysis.

Preparation of 2-Octyne.—This compound was obtained by the action of methyl iodide on sodium amylacetylide in liquid ammonia: b. p. 132-136°; d^{32} 0.751; n^{32}_D 1.4227.

Reaction of 2-Octyne with Methyl Alcohol.—The catalyst was prepared by heating together momentarily 3 g. of red mercuric oxide, 1 ml. of $(C_2H_5)_2O{\cdot}BF_3$, 0.5 g. of trichloroacetic acid, and 3 ml. of methyl alcohol. The reaction was carried out and the product purified as previously described.[1] From 55 g. of 2-octyne there was obtained 48 g. of 3,3-dimethoxyoctane: yield, 55%; b. p. 90-92° at 26 mm.; d^{25} 0.8552; n^{25}_D 1.4171; MR calcd. 51.67, found 51.22.

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(1) Hennion, Killian, *et al.*, THIS JOURNAL, **56**, 1130 (1934), and subsequent papers.

Anal. Calcd. for $C_{10}H_{22}O_3$: C, 68.89; H, 12.73. Found: C, 69.00; H, 12.79.

Hydrolysis of a 1-ml. sample yielded a ketone which was in turn converted to the semicarbazone. The latter melted at 112–113° which agrees with the value of 112° given by Pickard and Kenyon[2] for the semicarbazone of 3-octanone.

Reaction of Methoxy-4-butyne-2 with Methyl Alcohol.—A sample of this acetylene[3] was obtained through the courtesy of Dr. Wallace H. Carothers of E. I. du Pont de Nemours & Company to whom our sincere thanks are extended.

The catalyst was prepared as described above and the reaction carried out in the usual way. Forty-two grams of the acetylene yielded 42 g. of 2,2,4-trimethoxybutane, b. p. 67–69° at 30 mm.; yield, 57%. This compound has been obtained previously from vinylacetylene.[4]

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[2] Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1936 (1913).

[3] Jacobson, Dykstra and Carothers, THIS JOURNAL, **56**, 1169 (1934).

[4] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

CONTRIBUTION FROM THE
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NOTRE DAME, INDIANA

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p-Bromophenacyl Formate, a Solid Derivative of Formic Acid

BY CHARLES D. HURD AND ROBERT E. CHRIST

It was found by Judefind and Reid[1] that many aliphatic acids could be identified easily as their *p*-bromophenacyl esters. These solid esters made excellent derivatives for the acids. According to these authors, however, formic acid gave negative results. In contrast to this statement, we have found that formic acid behaves regularly. The preparation of *p*-bromophenacyl formate is a simple matter and the compound makes an admirable derivative. It melts at 140°.

One gram of sodium formate (solid) was dissolved in 5 cc. of water and 10 cc. of 95% alcohol. Then 1 g. of *p*-bromophenacyl bromide was added. The solution was boiled until nearly all the solvent had disappeared. More alcohol was added and it was boiled another half hour until the solvent had nearly disappeared. Finally, the product was dissolved in dilute alcohol and then cooled. The crystalline product was filtered and recrystallized from dilute alcohol. A total of 0.38 g. of product was obtained which possessed a melting point of 140°.

Equally good results were obtained by refluxing instead of boiling away the solvents. Then, the first amount of alcohol is sufficient.

Anal. Subs., 0.2027; AgBr, 0.1551. Calcd. for $C_9H_7O_3Br$: Br, 32.89. Found: Br, 32.56.

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[1] Judefind and Reid, THIS JOURNAL, **42**, 1052 (1920).

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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Optical Rotation Study of the New Orally Effective Principle of Ergot

BY E. C. KLEIDERER

Commercial production of the orally effective principle recently isolated from ergot has provided an adequate source for an intensive study of its properties.

The free base, called ergotocin by Kharasch and Legault, was crystallized from benzene and dried *in vacuo* for about eight hours. It melted at 157–158° (corr., bath at 150° when sample was introduced). The maleate salt was prepared from the crystalline base, and dried *in vacuo*.

The initial specific rotations of the free base in various solvents are given below. All rotations in this investigation were made in a one-decimeter tube at 28° unless otherwise stated. Due to the slight solubility of the base in cold chloroform and benzene, the rotations in these solvents were taken in a Landolt heating chamber.

TABLE I

Solvent	Wt. and vol. of solvent	α_D	$[\alpha]_D$
Distilled water	0.0276 g. in 10 cc.	+0.21°	+76.1°
Abs. methyl alcohol	.0485 g. in 15 cc. tube, 2 dm.	+ .26°	+40.2°
Cyclohexanol	.00659 g. in 1 cc. (micro)	+ .21°	+31.6°
Chloroform	.0179 g. in 10 cc.	− .08° at 50°	−44.7° at 50°
Benzene	.0164 g. in 10 cc.	− .10° at 75°	−61.0° at 75°

The rotation of the methyl alcoholic solution of the free base on standing at room temperature became more dextro as shown in Table II, while no change was observed on a water solution of the free base after standing at room temperature for one hundred hours.

TABLE II

Time, hr.	Initial	17	30	71.5	95.5
$[\alpha]^{28}_D$	+40.2°	+48.0°	+53.1°	+59.6°	+61.8°

The methyl alcohol was evaporated from the sample which had stood ninety-five and one-half hours, the residue recrystallized from benzene and the dried (*in vacuo*) product dissolved in