Anal. Calcd. for $C_{10}H_{22}O_2$: 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]

(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
CHEMICAL LABORATORIES OF THE
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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.

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

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

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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

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°

to the slight solubility of the base in cold chloroform and benzene, the rotations in these solvents were taken in a Landolt heating chamber.

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

water giving $[\alpha]^{28}D$ +95.4°. The melting point of the initial sample was 157–158° (dec.) and of the sample obtained from the 95.5-hour solution was 160–161° (dec.).

By the isolated rabbit uterus method,[1] the physiologic activity of the base obtained from the 95.5-hour sample was about 90% of that of the initial sample.

Initial rotations of the maleate salt of the new base were as follows.

TABLE III

Solvent	Wt. and vol. of solution	$\alpha^{28}D$	$[\alpha]^{28}D$
Distilled water	0.1042 g. in 10 cc.	+0.48°	+46.2°
Abs. methyl alcohol	.1017 g. in 25 cc.	+ .308°	+37.9°

Rotations were again made on these same solutions after standing at room temperature for forty-eight hours, and were found to be as follows: on the water solution $\alpha^{28}D$ +0.56°, $[\alpha]^{28}D$ +53.7°; on the methyl alcohol $\alpha^{28}D$ +0.20°, $[\alpha]^{28}D$ 24.6°. The forty-eight-hour methyl alcohol solution was evaporated *in vacuo* to dryness at room temperature, water was added to bring the solution up to the original methyl alcohol volume. The rotation was $\alpha^{28}D$ 0.214°, $[\alpha]^{28}D$ 52.9°. The physiologic activity of these forty-eight-hour samples as determined by the isolated rabbit uterus method was approximately the same as that of an initial sample.

The explanation of these results is not clear at present; evidently some change is occurring in the molecule which affects the optical rotation, but which does not greatly affect the physiologic activity. Changes of rotation have been noted in the cases of ergotinine and ergotamine which have been ascribed to a change into ergotoxine in the former case and into ergotaminine in the latter case. This explanation does not appear to be a logical one for the changes occurring here, since the physiologic activity seems to be practically unchanged and since the product obtained from a solution of the salt of the new base in methyl alcohol and the product obtained from a solution in water appear to be the same.

The author wishes to express his thanks to Dr. K. K. Chen and to Mr. E. E. Swanson of the Lilly Research Laboratories for their aid in determining the physiologic potency.

THE LILLY RESEARCH LABORATORIES
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(1) Davis, Adair, Chen and Swanson, *J. Pharmacol.*, **54**, 398 (1935); Swanson, Hargreaves and Chen, *J. Am. Pharm. Assoc.*, in press.

An Improved Method of Extraction

BY CHARLES A. MARLIES AND VICTOR K. LA MER

In an investigation on the acid and salt catalysis of nitramide,[1] NH_2NO_2, a novel method of extraction was employed in the final stage of the preparation of this interesting compound. In the customary method[2] the compound is extracted from its aqueous solution, some forty extractions with ether being necessary on account of the exceedingly unfavorable distribution ratio. The improvement consists of immersing the flask containing the nitramide solution and supernatant ether layer into a "dry ice" freezing mixture and swirling until the water layer solidifies completely. The nitramide passes into the ether layer which is decanted through a filter. Complete extraction was achieved by repeating the process three times. The yield obtained on evaporation of the four combined ether extracts was 80%, whereas the maximum yield by the previous method was but 25%, in agreement with the experience of Brönsted's laboratory.[3]

The low yields by the previous[2] method are probably due to decomposition during the prolonged evaporation of the large volume of ether. Nitramide is an extremely unstable substance and the catalytic action resulting from the concentration of the ever-present impurities (including water) during the evaporation probably causes considerable loss by decomposition.

This method of freezing the solvent during extraction should prove generally useful not only in cases where the distribution ratio is unfavorable but also to remove small amounts of material from large volumes of solution, provided, of course, that solid solution is not an important complication.

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NEW YORK, N. Y. RECEIVED JUNE 3, 1935

(1) Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).
(2) Thiele and Lachman, *Ann.*, **288**, 267 (1895).
(3) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); and a later private communication.