

## NOTES

## A Note on the Use of Methoxyacetic Anhydride for the Determination of Hydroxyl Groups

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The standard procedures for the determination of the presence and number of hydroxyl groups in organic compounds are methylation, followed by estimation of the methoxyl value, and acetylation, followed by estimation of the acetyl value. With the increasing use of micro-analysis the former is the better method since all who are familiar with the various methods of micro acetyl determination realize their unsatisfactory nature. The methoxyl determination, on the other hand, is readily performed but it suffers from the disadvantage that some compounds contain hydroxyl groups which are easily acetylated but which cannot easily be methylated. Into this group falls quercetin which readily yields a pentaacetyl derivative but gives a pentamethoxy derivative only with difficulty.<sup>1</sup> Penta-(methoxyacetyl)-quercetin is described later.

It appeared likely that the difficulties and uncertainties attending the acetyl determination might be eliminated largely by substituting the methoxy derivative for acetic anhydride in the acetylation reaction. The number of hydroxyl groups present in the original compound would then be determined from the methoxyacetyl derivative by estimating the methoxyl value. Up to the present time methoxyacetic anhydride has been difficult to obtain but it has now become commercially available<sup>2</sup> and the possibility of its use in place of acetic anhydride has therefore been realized. It appears to behave in the same manner as acetic anhydride and the methoxyacetyl derivatives described in the experimental part were all prepared in good yield by procedures in general use with acetic anhydride. In general, as might be expected, the compounds have lower melting points than the corresponding acetyl derivatives.

## Experimental

**Di-(methoxyacetyl)-hydroquinone (I).**—This compound was prepared by heating hydroquinone with methoxyacetic anhydride in pyridine solution for 0.75 hour. The solid precipitated by pouring into water was crystal-

(1) See Gomm and Nierenstein, *THIS JOURNAL*, **53**, 4408 (1931).

(2) A part of the anhydride used in this investigation was supplied by the firm of Dr. Fraenkel and Dr. Landau of Berlin, Oberschönweide, Germany.

lized first from alcohol and finally from petroleum ether (b. p. 60–80°) as fine colorless needles melting at 89.5–90°.

***p*-Methoxyacetoxybenzoic Acid (II).**—This was prepared in aqueous alkaline solution by the method of Chattaway.<sup>3</sup> It was crystallized first from aqueous alcohol and finally from alcohol as glistening colorless needles melting at 164–165°.

**Methoxyacetylchalcone (III).**—Prepared in ethereal solution with addition of anhydrous potassium carbonate according to the method of Malkin and Nierenstein.<sup>4</sup> After crystallizing from aqueous alcohol it was obtained from petroleum ether (b. p. 60–80°) as pale yellow needles which melted at 93°.

***p*-Methoxyacetoxyacetophenone (IV).**—Prepared by the method of Malkin and Nierenstein<sup>4</sup> and crystallized first from dilute acetone and then from petroleum ether (b. p. 40–60°) as colorless needles melting at 56–57°.

**Penta-(methoxyacetyl)-quercetin (V).**—This compound was obtained by gently boiling a solution of quercetin in methoxyacetic anhydride for four hours. The solution was then poured into water and the precipitated solid crystallized several times from a mixture of alcohol and acetone and finally from benzene. It was thus obtained as colorless needles melting at 97–98°.

## ANALYTICAL DATA

Subs.	Formula	Found, % (micro)			Calculated, %		
		C	H	OCH <sub>3</sub>	C	H	OCH <sub>3</sub>
I	C <sub>12</sub> H <sub>14</sub> O <sub>6</sub>	56.89	5.56	23.70	56.69	5.51	24.30
II	C <sub>10</sub> H <sub>10</sub> O <sub>5</sub>	57.26	4.74	14.40	57.14	4.76	14.76
III	C <sub>15</sub> H <sub>16</sub> O <sub>4</sub>	72.82	5.43	10.15	72.90	5.40	9.81
IV	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>	63.72	5.86	14.40	63.46	5.77	14.90
V	C <sub>30</sub> H <sub>30</sub> O <sub>17</sub>	54.26	4.62	22.60	54.38	4.53	23.31

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**Summary.**—Methoxyacetic anhydride is suggested as a substitute for acetic anhydride in the estimation of hydroxyl groups. Some methoxyacetyl compounds are described.

(3) Chattaway, *J. Chem. Soc.*, 3495 (1931).(4) Malkin and Nierenstein, *THIS JOURNAL*, **53**, 239 (1931).

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Preparation of Picolinic Acid Amide from  $\alpha$ -BromopyridineBY WALLACE R. BRODE AND CLARENCE BREMER<sup>1</sup>

In a recent article Craig<sup>2</sup> has described the preparation of  $\alpha$ -pyridyl cyanide from  $\alpha$ -bromopyridine. Attempts on our part to prepare this

(1) An abstract of a portion of a thesis presented by Clarence Bremer in partial fulfillment for the degree of Doctor of Philosophy in Chemistry at The Ohio State University, June, 1933.

(2) Craig, *THIS JOURNAL*, **56**, 231 (1934).