lized from alcohol. There was obtained 1.45 g. (74%) of **4,7-dihydroxy-2,3,3-triphenylindanone (VI)**, pale yellow needles, m. p. 183.5–185°. In concd. sulfuric acid, the compound gave only a greenish yellow solution.

Anal. Calcd. for $C_{27}H_{20}O_3$: C, 82.7; H, 5.1; mol. wt., 392. Found: C, 82.8; H, 5.3; mol. wt. (cryoscopic in benzene), 392.

The same compound was obtained in a yield of 92% when a solution of 1.0 g. of 4,7-dimethoxy-2,3-diphenylindone in 50 ml. of benzene containing 1.6 g. of aluminum chloride was boiled for ten minutes. This preparation helped to establish the structure of the substance.[3]

When 0.5 g. of VI was boiled for seventy-five minutes with 5 ml. of acetic anhydride containing 0.1 g. of sodium acetate, it gave 0.6 g. of **3,4,7-triacetoxy-1,1,2-triphenylindene,** colorless prisms from acetic acid, m. p. 219.5–220.5°.

Anal. Calcd. for $C_{33}H_{26}O_6$: C, 76.5; H, 5.0. Found: C, 76.4; H, 5.0.

A stirred solution of 0.5 g. of VI in 8 g. of methyl sulfate was treated with 20 ml. of 20% potassium hydroxide in small portions. The neutral product (0.53 g., m. p. 150–180°) was crystallized from alcohol, giving 0.32 g. of **4,7-dimethoxy-2,3,3-triphenylindanone,** colorless prisms, m. p. 196–198°.

Anal. Calcd. for $C_{29}H_{24}O_3$: C, 82.8; H, 5.7; OCH_3, 14.8. Found: C, 83.1; H, 5.8; OCH_3, 15.0.

The dimethyl ether dissolved with difficulty in methyl alcoholic alkali, forming a bright yellow solution, but it could not be methylated further.

(3) *Cf.* Koelsch, *J. Org. Chem.*, **3**, 456 (1938).

Summary

Phenylmagnesium bromide usually adds 1,2 to the carbonyl group in 2,3-diarylindones, but its reaction with 4,7-dihydroxy-2,3-diphenylindone yields 4,7-dihydroxy-2,3,3-triphenylindanone, a 1,4-addition product. An explanation for this behavior is suggested.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Behavior of γ-Keto- and Aldehydo-Acid Derivatives at the Dropping Mercury Electrode. III. 3-(*p*-Bromobenzoyl)-3-methylacrylic Acid Derivatives[1]

BY S. WAWZONEK, R. C. RECK, W. W. VAUGHT, JR., AND J. W. FAN

In previous work[1,2] the application of the dropping mercury electrode to structure determination of 2-benzoylbenzoic acid derivatives has been reported. Work of a similar nature has now been extended to the α,β-unsaturated γ-ketonic acid type in which there is a possibility of a *cis–trans* and cyclic form for the various derivatives.

In this paper the behavior of 3-(*p*-bromobenzoyl)-3-methylacrylic acid derivatives at the dropping mercury electrode will be presented. Structures in this series have been well established chemically by Lutz and co-workers.[3]

Results

The behavior of the various derivatives of 3-(*p*-bromobenzoyl)-3-methylacrylic acid and related compounds was studied in a 0.1 *M* tetrabutylammonium iodide–50% dioxane solution. The acids and examples of the typical structures occurring in this series were also studied in a 0.1 *M* tetrabutylammonium iodide, 0.052 *M* tetrabutylammonium hydroxide, 50% dioxane solution. A summary of the observed half-wave potentials and individual diffusion current constants is given in Table I.

In general all the compounds gave well-defined reduction waves. For compounds which gave indefinite waves, the total diffusion current together with an average half-wave potential is given. Maxima could be suppressed in most cases by means of 0.01% gelatin.

Discussion of Results

A comparison of the results obtained in the two solutions for the examples of the three characteristic structures in this series, indicates that the half-wave potentials are independent of *p*H. The only apparent effect of increasing the alkalinity of the solution is a slight change in the diffusion currents.

The acids because of their nature show a different behavior in the two solutions. In the alkaline solution in which they are present as anions, the reduction is normal. The *trans* acid gives three waves. The first wave, at −1.39 v., corresponds to a reduction to β-(*p*-bromobenzoyl)-butyric acid since the final two waves obtained at −1.60 and −1.79 v., are identical with the waves obtained for this acid. The last two waves correspond to the direct reduction of the ketone to the pinacol and the carbinol, respectively. A similar behavior has been observed in the reduction of acetophenone in alkaline solution.[4] The *cis* acid gives only two waves. The first wave, at −1.47 v., has an abnormally high diffusion current constant of 3.52 microamperes/millimole/liter/mg. $^2/_3$ sec.$^{-1}/_2$. This wave must include the reduction of the double bond and the reduction of the ketone to the pinacol because the second wave, at −1.77 v., is the normal reduction of the ketone group to the carbinol. This behavior would point to an open form for the anion

(1) Paper II: THIS JOURNAL, **66**, 830 (1944).

(2) Wawzonek, *et al.*, *ibid.*, **66**, 827 (1944).

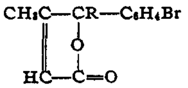
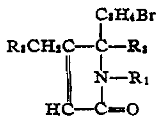
(3) (a) Lutz and Taylor, *ibid.*, **55**, 1168 (1933); (b) Lutz and Winne, *ibid.*, **56**, 445 (1934); (c) Lutz and Hill, *J. Org. Chem.*, **6**, 175 (1941).

(4) Wawzonek and Laitinen, THIS JOURNAL, **63**, 2341 (1941).

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS FOR 3-(*p*-BROMOBENZOYL)-3-METHYLACRYLIC ACID DERIVATIVES AND RELATED COMPOUNDS IN VARIOUS SOLUTIONS AT 25°

0.1 *M* Tetrabutylammonium Iodide–50% Dioxane

Compound	$\pi_{1/2}$ vs. S. C. E., volts	i_d, microamperes	*C*, millimoles/liter	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
$CH_3CCOC_6H_4Br$	−0.91	2.08	1.89	0.56
‖	−1.36	1.34		0.36
HCCOR	−1.55	5.84		1.57
R = OH	−1.80	5.96		1.60
	−1.49[a]	10.86[a]	1.56[a]	3.52[a]
	−1.77[a]	4.69[a]		1.52[a]
R = OCH_3	−1.19	4.45	1.07	2.10
	−1.57	4.40		2.08
	−1.73	2.10		0.99
R = $N(CH_3)_2$	−1.31	4.41	1.14	1.97
	−1.59	3.44		1.54
	−1.74	2.20		0.97
	−1.30[a]	3.45[a]	1.08[a]	1.62[a]
	−1.55[a]	3.68[a]		1.73[a]
	−1.79[a]	1.88[a]		0.88[a]
R = $N(CH_3)C_6H_5$	−1.23	6.30	1.58	2.02
	−1.59	4.35		1.40
	−1.76	4.33		1.39
$CH_3CCOC_6H_4Br$	−0.96	2.21	1.15	0.98
‖	−1.51	3.39		1.50
RCOCH	−1.79	1.47		0.65
R = OH	−2.32	2.54		1.13
	−1.39[a]	4.10[a]	1.10[a]	1.91[a]
	−1.60[a]	3.15[a]		1.45[a]
	−1.79[a]	2.18[a]		1.30[a]
R = OCH_3	−1.03	4.99	1.25	2.02
	−1.55	3.95		1.60
	−1.74	2.58		1.04
R = NHC_6H_5	−1.06	4.42	1.09	2.06
	−1.53	3.04		1.41
	−1.67	2.48		1.16
R = $N(CH_3)C_6H_5$	−1.13	5.30	1.26	2.13
	−1.59	4.06		1.63
	−1.74	3.48		1.40
				
R = OCH_3	−1.71	4.85	1.18	2.08
R = $N(CH_3)C_6H_5$	−1.01	3.02	0.83	1.86
	−0.96[a]	0.67[a]	0.98[a]	0.35[a]
	−1.50[a]	4.69[a]		2.43[a]
	−1.79[a]	1.98[a]		1.02[a]
R = NHC_6H_5	−0.99	2.11	1.17	0.91
	−1.63	2.24		0.97
	−2.34	4.58		1.99
β-(*p*-Bromobenzoyl)-butyric acid	−1.34	2.82	1.54	0.93
	−1.68	8.86		2.92
	−1.55[a]	6.40[a]	1.27[a]	2.55[a]
	−1.74[a]	3.22[a]		1.29[a]
				
$R_1 = R_3 = H$	−2.02	10.53	1.38	3.87
$R_2 = OH$	−2.44	4.76		1.75
	−2.10[a]	5.88[a]	1.09[a]	2.72[a]
	−2.35[a]	0.91[a]		0.42[a]
$R_1 = R_3 = H$	−2.01	11.63	1.47	4.01
$R_2 = OCH_3$	−2.50	3.83		1.35
$R_1 = R_2 = R_3 = H$	−2.07	6.95	1.60	2.20
	−2.40	7.10		2.26
$R_1 = H, R_2 = OH$	−1.85	6.29	1.26	2.53
$R_3 = Cl$	−2.27	4.68		1.89
$R_1 = H, R_2 = OCH_3$	−1.77	4.51	0.88	2.59
$R_3 = Cl$	−2.23	4.68		2.68
$R_1 = CH_3, R_2 = OH$	−2.23	15.41	1.12	6.95
$R_3 = H$				
$R_1 = CH_3, R_2 = OCH_3$	−1.94	5.36	1.50	1.76
$R_3 = H$	max.	14.21		4.78
$R_1 = CH_3, R_2 = R_3 = H$	−2.30	13.7	1.55	4.47
$R_1 = CH_3, R_2 = OH$	−2.13	14.65	1.04	7.14
$R_3 = Cl$				
$R_1 = CH_3, R_2 = OCH_3$	−1.78	5.79	1.16	2.53
$R_3 = Cl$	−2.22	12.10		5.28
$R_1 = C_6H_5, R_2 = OH$	−1.89	3.88	1.52	1.30
$R_3 = H$	−2.23	6.85		2.28
$R_1 = C_6H_5, R_2 = OCH_3$	−1.78	8.24	1.44	2.89
$R_3 = H$	−2.16	7.36		2.59
$R_1 = C_6H_5, R_2 = R_3 = H$	−2.23	7.30	0.99	3.75

[a] In 0.1 *M* tetrabutylammonium iodide, 0.052 *M* tetrabutylammonium hydroxide, 50% dioxane.

of the *cis* acid. The possibility of a cyclic structure, however, should not be disregarded. This form might open on reduction of the double bond to form a free ketone group and give the same type of behavior.

In neutral solution the behavior of the acids is difficult to interpret with certainty. Both acids, the *cis* (4.09) and *trans* (4.26) give a total diffusion current constant which is approximately equal to the total diffusion current constant of their reduction product, β-(*p*-bromobenzoyl)-butyric acid (3.85). Such a behavior points to the absence of a reduction wave for the double bond in each instance. This fact is substantiated by the half-wave potentials obtained. Waves at −1.55 and −1.75 v. in both cases point to the presence of the ketone group. In addition the *trans* acid shows a wave at −2.32 v. This wave must be involved in the reduction of the ketone group because a low diffusion current constant is obtained for the wave at −1.75 v. in comparison to that obtained for the *cis* acid. The waves at −0.91 and −1.36 v. for the *cis* acid and the wave at −0.96 v. for the *trans* acid have a total diffusion current constant, $i_d/Cm^{2/3}t^{1/6}$, of 0.92 and 0.98 microamperes/millimole/liter/mg.$^{2/3}$sec.$^{-1/2}$, respectively. They must correspond to the deposition of hydrogen since a wave of equal height (0.93) is shown by β-(*p*-bromobenzoyl)-butyric acid at −1.34 v. The two waves obtained for the *cis* acid point to an equilibrium between the cyclic and the open forms. A comparison of their diffusion current constants indicates that the forms are present in approximately the ratio of three to two. At the present time, however, there is no evidence to indicate which form is in excess.

One possible explanation for the absence of a reduction wave for the double bond in the *cis* and *trans* acids is that the double bond is hydrated in neutral or slightly acid solution. Supporting evidence for this behavior is the isolation by Lutz[3a] of a hydrate in the hydrolysis of the *trans* methyl

ester. Another possibility, that the deposited hydrogen reduces the double bond catalytically, is ruled out since only one-half the required amount of hydrogen would be produced in this way.

The behavior of the derivatives of the *cis* and *trans* acids in neutral solution is normal. All are reduced first at the double bond, for they show two final waves, characteristic of the ketone group. The *trans* form is reduced at more positive potentials than the *cis* form in all instances. This difference suggests the possibility of using the polarographic method to distinguish between such isomers when both forms are available. Values obtained for the *cis* N-dimethylamide confirm the open structure proposed by Lutz.[3c]

The cyclic methyl ester and cyclic N-methylanilide which have a furanone structure, show an entirely different behavior from the corresponding *cis* and *trans* compounds. Both are reduced to a dihydrofuranone since only one wave of two electrons is obtained. The appearance of additional waves at −1.50 and −1.79 v. for the cyclic N-methylanilide in alkaline solution points to a partial hydrolysis of this compound to the *cis* acid.

The anilide in the furanone series behaves differently from the cyclic methyl ester and N-methylanilide in neutral solution. It resembles the anil in the 2-benzoylbenzoic acid series,[1] giving two waves of approximately equal diffusion current constant, 0.91 and 0.97, at −0.99 and −1.63 v., respectively. These waves represent a reduction to a nitrogen-free compound since a third wave, identical to that found for the *trans* acid in neutral solution, is obtained at −2.34 v. This behavior is of interest since the anilide is converted by hydrochloric acid to the *trans* acid.[3c]

The remaining *cis* normal amides have a hydroxypyrrolinone structure, for they are reduced at slightly more negative potentials than their cyclic methyl ethers. Both of these derivatives in all instances are reduced to the corresponding 5 - (*p* - bromophenyl) - 4 - methyl - 2,5 - dihydropyrrolone-2. In each case where the individual half-wave potentials can be measured, the last two waves are identical with the waves obtained for the dihydropyrrolone.

Experimental

The current–voltage curves were determined in a manner similar to that described in the first paper in this series.[2] All measurements were made in a water thermostat at 25 ± 0.1°.

The dropping mercury electrode had the following characteristics. At a pressure of 46.5 cm. of mercury, the drop time in the solvent used was 3.34 seconds (open circuit). The value of m was 2.05 mg. sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 1.973 mg.$^{2/3}$ sec.$^{-1/2}$.

Materials.—The solutions used had the following compositions and anode potentials: 0.1 *M* tetrabutylammonium iodide, 50% dioxane, anode potential, −0.400 v.; 0.1 *M* tetrabutylammonium iodide, 0.052 *M* tetrabutylammonium hydroxide, 50% dioxane, anode potential, −0.393 v.

The compounds used in this work were prepared by methods given by Lutz and co-workers.[3]

Summary

The polarographic method is a suitable means of distinguishing between the *cis*, *trans* and cyclic derivatives of a typical α,β-unsaturated γ-ketonic acid, 3-(*p*-bromobenzoyl)-3-methylacrylic acid.

An explanation is offered for the anomalous behaviors of the *cis* and *trans* acids in neutral solution.

IOWA CITY, IOWA RECEIVED MAY 7, 1945

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1001]

Studies on the N-Acetyl-*d*-glucosylamine of Hockett and Chandler[1]

BY CARL NIEMANN AND JOHN T. HAYS[2]

In 1940 Hockett and Chandler[3a] announced the discovery of a second N-acetyl-*d*-glucosylamine $(\alpha)_D$ 87°, and in a recent communication[3b] suggested that this compound, which is isomeric with the previously described N-acetyl-*d*-glucosylamine $(\alpha)_D$ −22°,[4] is a N-acetyl-*d*-glucofuranosylamine. Hockett and Chandler obtained this new N-acetyl-d-glucosylamine $(\alpha)_D$ 87° by the reaction of either *aldehydo-d*-glucose pentaacetate or hexaacetyl-*d*-glucoheptonic nitrile with aqueous ammonia, the yield being approximately 56% in the first instance and 26% in the second.[5] We have found that this new N-acetyl-*d*-glucosylamine $(\alpha)_D$ 87° can also be prepared by the reaction of β-*d*-glucose pentaacetate with methanolic ammonia. In spite of the low yield (8%) this reaction is of considerable interest, not only in respect to the formation of N-acylglycosylamines of the above type, but also because alcoholic am-

(1) Taken in part from the Ph.D. Thesis of J. T. Hays, California Institute of Technology, June, 1942.

(2) Present address, Hercules Experiment Station, Wilmington, Delaware.

(3) (a) R. C. Hockett and L. B. Chandler, Division of Organic Chemistry, Cincinnati Meeting, American Chemical Society, April 1940; (b) THIS JOURNAL, **66**, 957 (1944).

(4) (a) P. Brigl and H. Keppler, *Z. physiol. chem.*, **180**, 38 (1929); (b) C. Niemann and J. T. Hays, THIS JOURNAL, **62**, 2960 (1940).

(5) We have observed that the substitution of methanolic ammonia for aqueous ammonia does not significantly alter the yield of the first reaction.