eter to avoid polarization and difficulties caused by high resistance of the cell. Potentials were measured at 27° between a saturated calomel electrode and a bright platinum electrode; the latter was immersed in an equimolecular mixture of quinone and hydroquinone at a concentration of about 4×10^{-5} molar in buffers prepared according to Conant and Chow.[3] The data are presented in Table I. From graphs of these data, values of E^0_h at $(p\text{H})_{\text{AcOH}} = 0$ were determined. They are, for benzoquinone, 0.650 v.; for I, 0.623 v.; for II, 0.835 v.

TABLE I

POTENTIOMETRIC MEASUREMENTS

Quinone	Buffer[a]	$(p\text{H})_{\text{AcOH}}$	E^0_h, v.[b]
Benzoquinone	1	4.24	0.408
	3	2.38	.528
	10	−0.98	.703
I	1	4.24	.371
	3	2.38	.488
	6	1.00	.571
	10	−0.98	.670
II	1	4.24	.588
	3	2.38	.703
	6	1.00	.784
	10	−0.98	.883

[a] Buffer numbers correspond to those used by Conant and Chow. [b] $E^0_h = E_{\text{cell}} + 0.098$ v.

Potentiometric titration at 28° of 20 ml. of a solution of the hydroquinone corresponding to I (13.1 mg., 75 ml. of alcohol, 0.7 g. of lithium chloride, 4.0 ml. of concd. hydrochloric acid, and sufficient water to make 100 ml.) with 0.0139 *N* ceric sulfate gave a curve (end-point, 1.44 ml. oxidant) at the mid-point of which $E = E_{\text{cell}} + E_{\text{s.c.e.}} = 0.398 + 0.246 = 0.644$ v. Titration of a similar solution of benzohydroquinone gave a curve (end-point, 1.41 ml. oxidant) with mid-point $E = 0.687$ v., whence, using 0.710 v.[13] as E_0 for benzoquinone in 75% alcohol at 28°, the *p*H at the mid-point was 0.4. With $E = E_0 - \frac{RT}{F}p\text{H}$, and assuming the mid-point *p*H to be the same in both titrations, I had $E_0 = 0.668$ v. in 75% alcohol.

Summary

Three methods of synthesizing 4,7-dimethoxy-2,3-diphenylindone are described. Demethylation of this substance and oxidation of the resulting dihydroxy compound yields 1-keto-2,3-diphenylindene-4,7-quinone. The quinone is yellow and presumably polymeric in the solid state, but its solutions are red and contain the monomer. It readily forms a 1:1 adduct with cyclopentadiene, and it has the high oxidation potential of 0.835 v.

[13] Conant and Fieser, THIS JOURNAL, **44**, 2489 (1922).

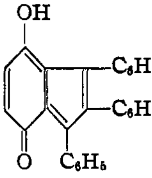
MINNEAPOLIS, MINNESOTA RECEIVED APRIL 30, 1945

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

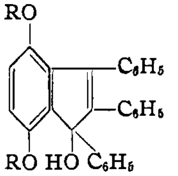
The Reaction of Phenylmagnesium Bromide with 4,7-Dihydroxy-2,3-diphenylindone[1]

BY C. F. KOELSCH AND E. J. PRILL

In order to investigate the possibility of forming a trans-nuclear quinoid compound (I) related to indene, it was desired to obtain 1,2,3-triphenylindenetriol-1,4,7 (II). The project had to be abandoned, however, for II could not be prepared either by demethylation of 4,7-dimethoxy-1,2,3-triphenylindenol-1 (III),[2] or by the action of phenylmagnesium bromide on 4,7-dihydroxy-2,3-diphenylindone.

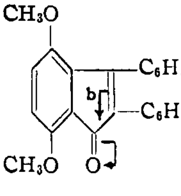


I

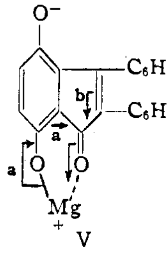


II, R = H
III, R = CH3

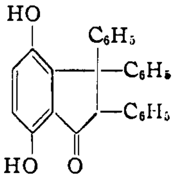
Demethylation failed because of the formation of tarry substances from III and strong acids. The Grignard synthesis failed because only 1,4-addition occurred, giving VI. This 1,4-addition was surprising in view of the exclusive 1,2-addition of phenylmagnesium bromide to all 2,3-diarylindones hitherto studied. But formulas IV and V indicate a possible explanation for the difference in behavior of the two compounds represented.



IV



V



VI

In IV, process b is weakened by conjugation with the phenyl groups, and the principal cationoid center is developed on C_1. In V, however, the cationoid properties of C_1 are largely neutralized by the strong resonance a, leaving C_3 as the main, even though still weak, cationoid center.

Experimental

No new C–C linkage was formed when phenylmagnesium bromide reacted with 4,7-dihydroxy-2,3-diphenylindone in ether, and decomposition of the complex gave back the indone. The reaction was carried out under forcing conditions. A warm solution of 1.57 g. of the indone in 100 ml. of toluene was treated with 12 ml. of 2 *N* phenylmagnesium bromide. The mixture was boiled for fifteen minutes, and then decomposed with iced acid. The solvents and biphenyl were removed with steam in the presence of a little sodium hydrosulfite, and the residue was crystal-

(1) From the Ph.D. Thesis of E. J. Prill, July, 1941.

(2) Koelsch and Prill, THIS JOURNAL, **67**, 1296 (1945).

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.

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.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 30, 1945

---

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

[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).