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CORRELATION BETWEEN THE REACTION OF KETONES WITH ZINC AND THEIR POLAROGRAPHIC HALF-WAVE REDUCTION POTENTIAL

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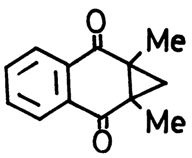
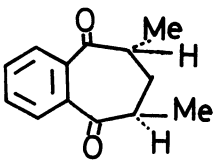
Correlation between the result on the reaction of ketones with zinc dust in acetic acid and their polarographic half-wave reduction potential in organic solvents is described.

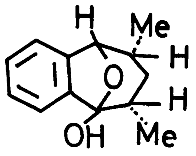
It has long been well-known that α-haloketones and unsaturated diketones in which the double bond is located between two carbonyl groups are easily reduced with zinc dust in acetic acid to give saturated ketones.[1] In addition to these facts we earlier published the study on the reduction of the diketone (1a) under similar conditions to afford the hemiacetal (1') by way of the diketone (1b) as an isolable intermediate.[2] The pathway for the reduction and their stereochemistry were also discussed. In this communication we wish to report the correlation between the results on reduction of ketones under the above reaction conditions and their polarographic half-wave reduction potentials in dimethyl sulfoxide or in acetonitrile.



(1a)

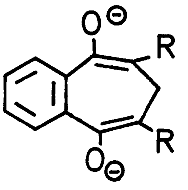


(1b)

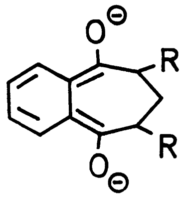


(1')

A series of ketones, (1) - (13), were subjected to reduction with zinc dust in acetic acid at room temperature. Some ketones, (9) - (13), did not react with zinc under the conditions, but a number of diketones, (1) - (8), readily underwent reduction to give hydroxyketones, (1') - (7'), or dibenzoylpropane (8') in fairly good yields as shown in Tables 1 and 2. For the purpose of explaining the experimental results an enolate such as 1c or 7c is assumed as the reduction

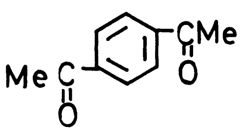
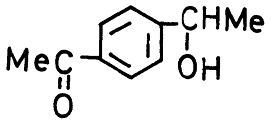
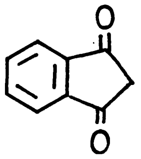
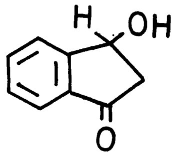
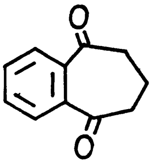
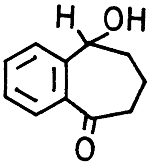
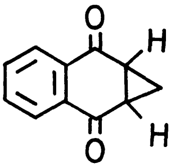
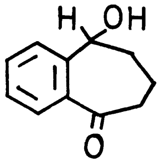
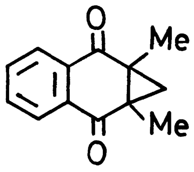
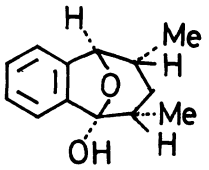


(1c) R : Me



(7c) R : H

Table 1 Results of the reduction and half-wave reduction potential*

Diketones		Products		Yields	$-E_{1/2}$**	Solvent***
Biacetyl	(2)	Acetoin	(2')	51	1.28	DMF
1-Phenylpropane-1, 2-dione	(3)	α-Acetylbenzyl alcohol	(3')	62	1.18	DMF
Benzil	(4)	Benzoin	(4')	77	1.18	DMF
trans-Dibenzoyl-cyclopropane	(8)	1, 3-Dibenzoyl-propane	(8')	85	1.48	DMF
	(5)		(5')	76	1.55	DMF
	(6)		(6')	83	1.31	DMF
	(7b)		(7')	76	1.59	DMF
	(7a)		(7')	68	1.40	ACN
	(1a)		(1')	63	1.45	ACN
Benzophenone	(15)	Benzopinacol	(15')	81	1.55	DMF

* The half-wave potentials were obtained on a Yanagimoto PA 102 Polarograph.

** The potentials are shown in - V vs saturated KCl / Hg for the first wave.

*** Tetraethylammonium perchlorate was used as the supporting electrolyte in dimethylformamide (DMF) and tetramethylammonium bromide was used in acetonitrile (ACN).

Table 2 Half-wave reduction potentials of ketones which can not be reduced by zinc dust in acetic acid at room temperature*

Ketones		$-E_{1/2}$ (V)	Solvent
Acetophenone	(9)	2.01	DMF
Propiophenone	(10)	2.01	DMF
m-Diacetylbenzene	(11)	1.81	DMF
1, 5-Diacetylnaphthalene	(12)	1.59	DMF
p, p'-Diacetylbiphenyl	(13)	1.82	DMF
Methyl p-acetylbenzoate	(14)	1.61	DMF

* Cf. the footnotes in Table 1.

intermediate. Ketonization of 7c should result in formation of a hydroxyketone as though just one of two carbonyl groups would be selectively reduced. This interesting conversion might be useful for the reduction of o- or p-diacylbenzene derivatives in organic synthesis. Treatment of 1a with zinc dust in acetic anhydride gave a mixture of 1b and the acetate of 1c almost in equal amount based upon its n. m. r. spectrum.

A structural feature for the diketones, (1) - (8), apparently consists in a conjugated system between two carbonyl groups or a homoconjugated system through a cyclopropane ring. In these diketones electron transfer from the metal becomes much easier, since anion radicals of such conjugated π -electron systems are obviously stabilized in comparison with that of the other ketones, (9) - (13). Streitwieser clearly showed the linear relationship between the energy of the lowest vacant orbital and the polarographic half-wave reduction potential for conjugated aromatic hydrocarbons.[3] Also it has been pointed out that the products of electrolytic reduction parallel those of reduction with metals.[4]

In connection with these relationships, the half-wave reduction potentials of the ketones in mercury electrode polarography were measured in dimethylsulfoxide and acetonitrile in order to compare with the above experimental results. As seen in the Tables 1 and 2, all the ketones, (1) - (8), which were reduced with zinc dust showed $-E_{1/2}$ values lower than 1.59 V vs sat. KCl / Hg, while the ketones, (9) - (13), which were recovered intact showed higher values than that. Namely, it is expected that the carbonyl compounds which showed $-E_{1/2}$ values lower than 1.59 V will be reduced with zinc dust in acetic acid at room temperature to give the products depending on their structural characteristics. Additional evidences for this anticipation were obtained in other two cases. The $-E_{1/2}$ value of benzophenone (15) was 1.55 V and it was reduced by this procedure to produce benzopinacol (15') in high yield, though methyl p-acetylbenzoate (14) showed 1.61 V and did not react under the conditions.

The order of the relative ease of reduction for some diketones was estimated by means of the following competitive experiments. A mixture of given two diketones in acetic acid was reduced with zinc dust at room temperature. An aliquot was analyzed by vapor phase chromatography at constant intervals with a view to obtaining both the consumption rates of two reactants and production rates of reduced compounds. Thus, the decreasing order of the reactivity was 6 > 7a > 1a > 8 > 7b. This order is again in accordance with that of polarographic half-wave reduction potentials of these diketones fairly well. The high reactivity of indanedione (6) in the reduction is presumably owing to the generation of aromatic 10-π-electron system as a result of electron transfer. With regard to the reductive opening mode of a cyclopropane ring of homonaphthoquinones (1a and 7a), it may be deduced from the above relative order that a dienolate (1c) is formed as the first intermediate by the direct opening of the cyclopropane, followed by diketonization to diacylbenzene derivatives (1b or 7b), which then undergo reduction into the second dienolate (7c) giving the final product (1' or 7'). This opening mode is in remarkable contrast to the result on the alicyclic system reported by Wenkert and Yoder.[5]

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