

ried out with hydrochloric acid in dilute alcohol in the presence of *p*-nitrophenylhydrazine a compound whose properties and melting point agree with those of the bis-*p*-nitrophenylhydrazone of succinaldehyde⁹ was obtained.

Experimental

cis-2,5-Dicarboxytetrahydrothiophene.—This was prepared from *meso*-dibromoadipic acid¹⁰ by the method of Fredga,¹¹ who reported a melting point of 144–145°. The product obtained by us softened at 135° and melted at 141–143°, but it possessed the expected composition.

Anal. Calcd. for C₆H₈O₄S: C, 40.90; H, 4.58. Found: C, 40.79; H, 4.98.

Diethyl Ester of 2,5-Dicarboxytetrahydrothiophene.—Ten grams of the acid was dissolved in 150 ml. of absolute ethanol and the solution saturated with dry hydrogen chloride and refluxed two hours. The solution was concentrated *in vacuo*, was dissolved in 75 ml. of ether, and was washed twice with saturated sodium bicarbonate. The ether solution was dried over sodium sulfate and distilled. The product distilling at 157° at 10 mm. amounted to 11.2 g. (85%).

2,5-Dicarboxytetrahydrothiophene Dihydrazone.—Three grams of the above ester in 9 ml. of ethyl alcohol was warmed to about 70° and 1.74 g. of 100% hydrazine hydrate was added. A green color developed and faded in five minutes. The solution was allowed to crystallize at room temperature overnight. The product was re-

crystallized from alcohol and yielded 600 mg. (23%) of needles melting at 208–209°.

Anal. Calcd. for C₈H₁₂O₂N₄S: N, 27.42. Found: N, 27.24.

2,5-bis-(Carbethoxyamino)-tetrahydrothiophene.—To 200 mg. of the above hydrazide in 5 ml. of 1 *N* hydrochloric acid, cooled to 0°, was added a layer of 5 ml. of ether, and 138 mg. of sodium nitrite in 1.4 ml. of water was added dropwise during five minutes with shaking and cooling. The ether layer was separated and the water was extracted twice with 5-ml. portions of cold ether. The ether extract was dried over sodium sulfate and concentrated *in vacuo*. To the cold diazide was added 50 ml. of absolute alcohol. The solution was warmed slowly in a water-bath. At about 50°, micro-bubbles of gas were evolved and heating was continued until the alcohol boiled gently. The alcohol solution was concentrated and the residue was recrystallized from 20% alcohol yielding 120 mg. (53% yield) of crystals melting at 152–154°.

Anal. Calcd. for C₁₀H₁₈O₄N₂S: C, 45.78; H, 6.92; N, 10.68; S, 12.22. Found: C, 45.90; H, 6.88; N, 10.53; S, 12.14.

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Summary

The synthesis of 2,5-bis-(carbethoxyamino)-tetrahydrothiophene has been accomplished. It has been shown that it is readily hydrolyzed to yield ammonia, hydrogen sulfide and succinaldehyde.

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(9) C. Harries and H. Krützfeld, *Ber.*, **39**, 3670 (1906).

(10) B. Holmberg and E. Müller, *ibid.*, **58**, 1601 (1925).

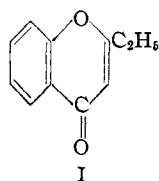
(11) A. Fredga, *J. prakt. Chem.*, **180**, 124 (1938).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Oxidation Potentials of Methoxyacetophenones

BY ROBERT H. BAKER AND JACK G. SCHAFER

It has been observed¹ that 2-ethylchromone, I, is not reduced by the Meerwein-Ponndorf method.



It seems logical to account for this behavior on the basis of the fact that the compound is a vinylog of an ester. Although esters suffer alkoxyl exchange with aluminum alkoxides, they are not reduced even under forcing conditions.² Open chain vinylogs of esters have also been

found to resist such reduction,¹ but it appeared that if the vinyl group is contained in an aromatic nucleus the compound should have properties intermediate between those of esters and ketones.

It has been possible to combine *o*-, *m*- and *p*-methoxyacetophenones with fluorenone in the presence of aluminum *t*-butoxide according to the equation, acetophenone + fluorenone \leftrightarrow methylphenylcarbinol + fluorenone. Since the normal potential of fluorenone is known,³ the determination of the concentrations at equilibrium in such reactions allows the assignment of normal potentials to these ketones. The normal potential of acetophenone is 151 mv.³ and that of *m*-methoxyacetophenone, which is not an ester vinylog, is

(1) This will be reported in a forthcoming publication.

(2) Baker, *THIS JOURNAL*, **60**, 2673 (1938).

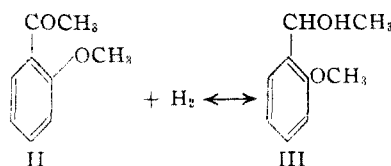
(3) Baker and Adkins, *ibid.*, **62**, 3305 (1940).

only slightly different, 158 mv. The other isomers being ester vinylogs were expected to have lower potentials. This is true for the para isomer, 129 mv., but is not so for the ortho, 160 mv. The free energies of reduction, calculated from the formula $-\Delta F = nFE_0$, and the normal potentials are compared with acetophenone in Table I.

TABLE I
CALCULATED CONSTANTS

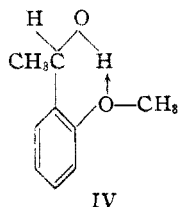
Acetophenone	% Fluorenone at equil.	E_0 , mv.	$-\Delta F$, kcal.
Unsubstituted	50	151	7.0
<i>o</i> -Methoxy	60	160	7.4
<i>m</i> -Methoxy	57	158	7.3
<i>p</i> -Methoxy	28	129	6.0

The 1.4 kcal. difference in the free energies of reduction of the *o*- and *p*-isomers must be accounted for either on the basis of a lesser stability of the ketone II or a greater stability of the carbinol III relative to their para isomers.



Blocking effects of the methoxyl group would be expected to affect both the alcohol and ketone, therefore it seems best to account for a stabilizing of the carbinol through hydrogen bonding.

If it is assumed that in solutions as dilute as those investigated, about 0.025 molar in any one reactant, intermolecular hydrogen bonding is negligible the greater decrease in free energy of reduction of the ortho over the para isomer may be attributed to the strength of the intramolecular O-H-O bond in the carbinol IV.



Since the unshared pair of electrons on the methoxyl oxygen are conjugate with the aromatic nucleus, this O-H-O bond would be expected to be weaker than in aliphatic alcohols, 6.2 kcal./mole.⁴ and probably comparable to the strength of the O-H-Cl bond in *o*-chlorophenol, 1.4 kcal./mole.⁴

(4) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp 289 ff.

Experimental

The ketones were equilibrated against fluorenone by the method previously described for acetophenone.³ The approach to equilibrium was followed by hydrolyzing aliquots of the reaction mixtures and measuring the heights of the respective ketone waves produced by a Sargent Model XI Polarograph. The empirical half-wave potentials of the ketones in aqueous isopropyl alcohol solutions containing tetramethylammonium hydroxide are: fluorenone, -0.99; *o*-, *m*- and *p*-methoxyacetophenone -1.80, -1.71 and -1.67 volts, respectively. All waves are of the characteristic doublet type in basic solution. The equilibration data are summarized in Table II.

TABLE II
MOLE PER CENT. OF FLUORENONE AT VARIOUS TIMES

Acetophenone	Hours				
	0	0.5	1.0	1.5	2.0
<i>o</i> -Methoxy	50	53		57	
	60		60		60 ^a
	70		64		60 ^a
<i>m</i> -Methoxy	50	53	57 ^a	56	59
	57	56	56 ^a	55	54
	74	63	58 ^a	59	58
<i>p</i> -Methoxy	20	23	24	27	26
	28	28	27	28	28 ^a
	53	43	34		32

^a These values used for the calculation of E_0 .

Preparation of Compounds.—All distillable reagents were carefully fractionated through either a 16-plate Stedman or a 4-plate micro Podbielniak column at reflux ratios well above the plate values. The samples for equilibration work were taken from the center of the fractions of constant refractive index.

o and *p*-methoxyacetophenone were prepared by individual methylations⁵ of the Fries rearrangement products⁶ of phenyl acetate. *m*-Methoxyacetophenone was obtained in an over-all yield of 4% by the following series of reactions: *m*-nitroacetophenone⁷ \rightarrow *m*-aminoacetophenone⁸ \rightarrow *m*-hydroxyacetophenone⁸ \rightarrow *m*-methoxyacetophenone.¹⁰ The carbinols were prepared by the hydrogenation of the respective ketones over copper-chromium oxide by established methods.¹¹ Other compounds were prepared according to methods already described.³

Summary

The oxidation-reduction potentials of *o*-, *m*- and *p*-methoxyacetophenones have been determined. The ester-like character of the *p* isomer is reflected in its low potential and the failure of the *o* isomer to show a similar low potential is ascribed to intramolecular hydrogen bonding in its reduced form.

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(5) Perkin and Weizmann, *J. Chem. Soc.*, **89**, 1649 (1906).

(6) Cox, *THIS JOURNAL*, **49**, 1028 (1927).

(7) We are indebted to Mr. T. R. Norton for a generous supply of this compound.

(8) Rupe, Braun and von Zembruksi, *Ber.*, **34**, 3522 (1901).

(9) Fuson, Lewis and Du Puis, *THIS JOURNAL*, **54**, 1114 (1932).

(10) Hiers and Hager, "Org. Syn.," 2nd ed., Coll. Vol. I, p. 58.

(11) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937.