several ways that in nitric acid solutions the oxidized silver is, within their experimental error, completely in the dipositive state. The concentration of dipositive silver in our solutions did not exceed 10^{-4} formal, which is much below its known solubility in similar solutions. Several requirements have to be met in order for the argentous–argentic system to be useful in secondary coulometric titrations. First, the current efficiency for the production of dipositive silver would have to be 100%; second, the rate of oxidation of reductants would have to be rapid, and, third, in order for an amperometric end-point to be used, the Ag(I)–Ag(II) couple would have to be reversible at the indicator electrodes.

Experiments were carried out with the apparatus described by Meier, Myers and Swift.[6] Argentic silver was anodically generated both in silver perchlorate solutions 1 to 6 formal in perchloric acid and in silver nitrate solutions 1 to 10 formal in nitric acid and it was found that the couple setup on the smooth platinum indicator electrodes was reversible, in that indicator currents were observed. It appeared that the anodic oxidation occurred with nearly 100% current efficiency, since after a brief initial delay period, the plot of the indicator current *vs.* generation time was linear.

Noyes, Coryell, Stitt and Kossiakoff[7] found that the rate of reduction of dipositive silver by water varied inversely with the concentration of nitric acid, and followed the rate law $\frac{-\mathrm{d}[\mathrm{Ag(II)}]}{\mathrm{d}t} = k_2 \frac{[\mathrm{Ag(II)}]^2}{[\mathrm{Ag(I)}]} + k_4 \frac{[\mathrm{Ag(II)}]^4}{[\mathrm{Ag(I)}]}$, with the second order term predominating at low dipositive silver concentrations. However, we found that if the indicator current was assumed to be proportional to the dipositive silver concentration, the rate of decomposition was first order with respect to the dipositive silver, and was many orders of magnitude faster than that observed by Noyes, *et al.* It can be shown that if the indicator current is proportional to any power of the dipositive silver concentration the observed first order decay ($\mathrm{d}i/\mathrm{d}t = ki$) of the indicator current requires the reduction of the dipositive silver to be first order. We also observed that the rate of decomposition varied directly as the acid concentration. These facts indicated that the mechanism of decomposition was different from that reported by Noyes, *et al.* We suspected that the decomposition was catalyzed by the platinum electrodes in the cell, and this was shown to be true by varying the electrode surface area; the rate of decomposition was directly proportional to the surface area of the platinum. This also explained the first order dependence on the dipositive silver concentration, in that the rate of decomposition was proportional to the rate at which the dipositive silver diffused to the platinum surface, and this rate was proportional to the concentration of dipositive silver in the cell.

In addition to the fairly rapid decomposition, another difficulty was encountered when it was found that an indicator current was not observable until after approximately four or five seconds of generation. At first it was thought that this was due to impurities in the solution which were being oxidized, but this was shown to be not true by varying the concentrations of the reagents, and also by generating a large amount of dipositive silver in the solution and then allowing it to decompose overnight. When this solution was again anodically oxidized, the same delay in obtaining an indicator current was noticed. The cause of this initial delay is uncertain. The period of delay was not constant, which would introduce a large uncertainty in the end-point corrections when using this system as a means of analysis.

Noyes, Hoard and Pitzer[5] reported that argentic silver solutions rapidly oxidized such substances as Mn(II), Cr(III), As(III) and Ce(III). However, we found that the rates of oxidation of all reducing agents tried, including Mn(II), As(III) and Ce(III), were much too slow to enable the coulometric method to be developed, since large indicating currents were observed before the equivalence point. The slow rates of oxidation were observed in both nitric and perchloric acid solutions of widely varied concentrations. This apparent anomaly is attributed to the extremely large Ag(I)/Ag(II) ratio in our solutions which would give a very low concentration of Ag(III) which was postulated to be the kinetically active specie by Noyes, Coryell, Stitt and Kossiakoff.[7]

The slow rate of oxidation of the above species, the variation in the initial delay of the indicator current, and the fairly rapid decomposition of the dipositive silver by water caused discontinuance of further work on the use of dipositive silver as a coulometric intermediate.

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An Improved Synthesis of 10-Thiaxanthenol

BY H. F. OEHLSCHLAEGER[1] AND IAN R. MACGREGOR

10-Thiaxanthenol is a somewhat unstable compound which has been prepared by reduction of thiaxanthone with zinc dust and alcoholic sodium hydroxide[2] or potassium hydroxide.[3,4] Hilditch and Smiles[5] reported erratic results, an impure

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[6] D. J. Meier, R. Myers and E. H. Swift, THIS JOURNAL, **71**, 2340 (1949).

[7] A. A. Noyes, C. D. Coryell, F. Stitt and A. Kossiakoff, *ibid.*, **59**, 1316 (1937).

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[2] Werner, *Ber.*, **34**, 3310 (1901).

[3] Mayer, *ibid.*, **42**, 1133 (1909).

[4] Finzi, *Gazz. chim. ital.*, **62**, 211–218 (1932).

[5] Hilditch and Smiles, *J. Chem. Soc.*, **99**, 145 (1911).

product, and a low yield using Mayer's method of reduction.[3]

Application of the method of "Organic Syntheses"[6] for the reduction of xanthrone to xanthydrol gave reasonably pure 10-thiaxanthenol in almost quantitative yield when thiaxanthone was used in place of xanthone. It was found to be more convenient to add sodium to a mixture of mercury and thiaxanthone suspended in alcohol rather than to add the thiaxanthone to sodium amalgam and alcohol.

A mixture of 375 g. of mercury, 13.8 g. (0.065 mole) of thiaxanthone and 80 cc. of 95% alcohol was placed in a pressure bottle. Small pieces of sodium (4.6 g., 0.2 mole) were added during a period of 15 minutes while the mixture was being shaken. The temperature of the mixture rose during addition of the sodium, and a dark purple color developed which gradually disappeared as all of the thiaxanthone went into solution. After the mixture had been shaken mechanically for an additional fifteen minutes, the alcohol layer was decanted. The mercury amalgam was washed with two 15-cc. portions of hot alcohol and the combined alcoholic solutions were filtered and poured into one liter of water. A white, finely crystalline precipitate was collected and air-dried. A yield of 13.4 g. was obtained (96.5%). The crystalline material melted at 103–104°, and was pure enough for subsequent reactions; a sample recrystallized from high boiling ligroin melted at 104–105°. 10-Thiaxanthenol is susceptible to air oxidation in light and should therefore be stored in a sealed brown bottle.

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[6] Holleman, "Organic Syntheses," Coll., Vol. I, p. 544, 1947.

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The Reaction of Dimethylcadmium with Cyclobutanecarboxylic Acid Chloride

BY REX PINSON, JR., AND S. L. FRIESS

In connection with a study of the reaction of acetylcyclanes with perbenzoic acid, it was necessary to prepare a supply of cyclobutylmethyl ketone (I). The compound has been prepared previously by the action of dimethylzinc[1] on cyclobutanecarboxylic acid chloride (II), but the undesirable properties of the zinc reagent made preferable the newer reaction of dimethylcadmium (III) with the acid chloride for the preparative step.

In a recent survey[2] of this reaction, it has been noted that, with respect to relative reactivity toward R_2Cd, the entire -COCl function is generally more reactive in a process of normal ketone formation than is its carbonyl moiety toward addition of the organometallic compound. As a result, little or no addition to the carbonyl (leading to carbinol formation) will occur unless it is unusually activated by some adjacent function. Furthermore, in acid chlorides possessing unusually high carbonyl activity, it has been observed[3] that carrying out the addition of the acid chloride to a solution of the organocadmium compound at a lower temperature than that of the refluxing solvent improves the yield of ketone.

In the present study, it has been found that a carbonyl group adjacent to a cyclobutane ring is highly reactive toward addition of cadmium reagent, and also reactive in certain other addition processes.[4] As a result of this reactivity, the customary procedures for the reaction, which employ a large excess[5] of cadmium reagent and dropwise addition of the acid chloride to an ethereal solution of dialkylcadmium held at the reflux temperature, furnish a product from II that is exclusively tertiary carbinol. This is presumably formed by a combination of normal reaction and carbonyl addition.

However, variation of conditions in the reaction of II with III has shown that the reaction may be stopped at the ketone stage, provided that (1) the addition of acid chloride is made to a well-stirred solution of the organometallic agent held at −70°; (2) the molar ratio of III to II is reduced to about 0.7; and (3) after stirring at −70° for one hour following completion of the addition of II, the reaction mixture is decomposed with water while still cold. Under these conditions, a yield of 66% (based on acid chloride) of I was realized.

A detailed description of the method using these optimum conditions, including a brief outline of the procedure for working up a reaction mixture containing a steam-volatile ketone, is given in the experimental section.

Experimental[6]

Various batches of the cyclobutanecarboxylic acid required for the reaction were prepared by the procedures of Heisig and Stodola,[7] Walborsky,[8] and Cason.[9] The acid chloride II was prepared from the acid by use of thionyl chloride, in a yield of 85%. Preparation of the dimethylcadmium reagent in absolute ether was carried out essentially according to the improved procedure of Cason.[2]

Optimum Reaction Conditions.—In a 1-l. three-necked flask fitted with stirrer, dropping funnel, and reflux condenser was prepared an ethereal solution of methylmagnesium iodide from 17.0 g. (0.71 mole) of magnesium turnings, 119 g. (0.84 mole) of methyl iodide, and a total of 375 ml. of absolute ether. The Grignard solution was cooled to 0° and 64 g. (0.35 mole) of anhydrous cadmium chloride (pulverized) added to it in small portions, with constant stirring, over a period of 45 minutes. The ice-bath was then removed and the solution stirred for one hour at room temperature, after which a Michler ketone test for residual Grignard reagent proved negative.

The dimethylcadmium solution was then cooled to ap-

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[1] (a) Perkin and Sinclair, *J. Chem. Soc.*, **61**, 47 (1892); (b) Zelinsky and Gutt, *Ber.*, **41**, 243 (1908).

[2] Cason, *Chem. Revs.*, **40**, 15 (1947).

[3] Ref. 2, p. 20.

[4] Friess and Pinson, unpublished work; the addition step in the reaction of I with perbenzoic acid is extremely rapid, as compared to the reaction rates of acetylcyclanes of larger ring size. Activation has been shown to be a function of the cyclic substituent, and not of the methyl group.

[5] In an excellent application of the reaction in the steroid series, using several times the theoretical amount of cadmium reagent, yields of methyl ketones as high as 95% were obtained; Julian, THIS JOURNAL, **67**, 1369 (1945).

[6] Melting points are corrected.

[7] Heisig and Stodola, "Organic Syntheses," Vol. 23, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 16.

[8] Walborsky, THIS JOURNAL, **71**, 2941 (1949).

[9] Cason, *J. Org. Chem.*, **14**, 1036 (1949).