solutions yellow, glassy melts result, and some decomposition occurs. These ions differ somewhat from the cobalticinium ion in being more difficult to precipitate from aqueous solution, even with very large anions. The following reagents, many of which precipitate the cobalticinium ion,[1] failed to precipitate the rhodicinium or iridicinium ions from solutions 1.0 to 10.0 mM in concentration: H_2PtCl_6, $K_3Co(NO_2)_6$, $KMnO_4$, $KClO_4$, picric acid, salicylic acid, potassium phthalimide, and various substituted naphthol sulfonic acids.

Polyiodides of both ions are obtained upon adding to solutions of at least 0.1 mM concentration a solution of iodide in sodium iodide. However, in contrast to the behavior of the cobalticinium ion with this reagent, no simple triiodides are obtained. Analyses on various samples indicated between five and seven iodine atoms per metal atom.

The addition of bromine water to solutions of at least one mM concentration produces flocculent orange precipitates. If these precipitates are then alternately washed with water and dried in a vacuum desiccator at room temperature, two or three times, pure salts of the tribromide ion Br_3^- result. *Anal.* Calcd. for $(C_5H_5)_2RhBr_3$: C, 25.40; H, 2.18; Br, 51.79. Found: C, 25.46; H, 2.18; Br, 50.68.

Reinecke's salt, $NH_4[Cr(CNS)_4(NH_3)_2]\cdot H_2O$, precipitates the rhodicinium and iridicinium ions from solutions of concentration 0.1 mM or higher. The resulting salts cannot be recrystallized from water because of the instability of the anion. They can be obtained in a quite pure state, however, by digesting them with water below 60° for several hours. *Anal.* Calcd. for $[(C_5H_5)_2Rh][Cr(CNS)_4(NH_3)_2]\cdot H_2O$: C, 29.52; H, 3.19; N, 14.76; S, 22.52; Rh, 18.1; Cr, 9.13. Found: C, 30.19; H, 3.23; N, 14.14; S, 22.81; Rh, 18.9; Cr, 9.16. Calcd. for $[(C_5H_5)_2Ir][Cr(CNS)_4(NH_3)_2]\cdot H_2O$: Cr, 7.74. Found: Cr, 7.93.

With a freshly prepared solution of dipicrylamine, the rhodicinium and iridicinium ions give scarlet precipitates which were recrystallized from acetone.

Anal. Calcd. for $[(C_5H_5)_2Rh][N(C_6H_2N_3O_6)_2]$: C, 39.35; H, 2.10; N, 14.61; Rh, 15.32. Found: C, 39.36; H, 2.06; N, 14.36; Rh, 15.87. Calcd. for $[(C_5H_5)_2Ir][N(C_6H_2N_3O_6)_2]$: C, 34.70; H, 1.85; N, 12.88. Found: C, 33.98; H, 1.94; N, 12.70.

Silicotungstic acid gives precipitates with acid solutions one mM or more in rhodicinium or iridicinium ions.

Solutions of the rhodicinium and iridicinium ions were treated with various oxidizing agents and in no case was there any evidence that they could be oxidized to cations of higher charge. The conclusion that no such higher oxidation states exist is corroborated by the absence of any polarographic oxidation waves in the region 0.0 to +0.5 v. *versus* S.C.E. The polarograms were made using neutral perchlorate solutions of the ions, concentration about millimolar, with 0.1 M sodium perchlorate as supporting electrolyte.

Polarographic study of a rhodicinium perchlorate solution in a 0.1 M sodium perchlorate supporting electrolyte at pH about 7 (also containing 0.05% gelatin to suppress a maximum which otherwise appeared) shows a cathodic wave at the dropping mercury electrode with a half-wave potential of −1.53 v. *versus* the S.C.E. Using the polarographic constant for the cobalticinium ion,[3] calculation shows that this wave represents a one-electron change, thus corresponding to the reduction of the rhodicinium ion to the neutral bis-cyclopentadienylrhodium(II) compound $(C_5H_5)_2Rh$. Like the neutral compound of cobalt(II), evidence for the existence of which has been obtained in the form of unstable easily oxidized solutions in organic solvents from the reaction of cobalt(II) acetylacetonate with cyclopentadienylmagnesium bromide,[4] the neutral compound $(C_5H_5)_2Rh$ cannot be isolated from aqueous solutions.

No reduction wave could be obtained for the iridicinium ion since even at a pH of 11 it is masked by a catalytic hydrogen wave. Solutions of Ir^{+3} and Ir^{+4} compounds are known to catalyze the reduction of hydrogen ion at the dropping mercury electrode, and in the present case the effect is probably due to similar action of the reduction or decomposition products formed from the iridicinium ion at the dropping mercury electrode.

Rhodicinium hydroxide was made in aqueous solution by the action of freshly prepared silver oxide on a solution of rhodicinium chloride. This solution was then titrated potentiometrically with 0.03 N hydrochloric acid using a Beckman Model G pH meter with glass and saturated calomel electrodes. From titration curves so obtained, the value of the dissociation constant of rhodicinium hydroxide was calculated to be 1.1×10^{-3}. Iridicinium hydroxide is a base of comparable magnitude.

The ultraviolet absorption spectra of the rhodicinium and iridicinium ions are shown in Fig. 1 together with the spectrum of the cobalticinium ion. Measurements at several wave lengths indicated that Beer's law is obeyed by solutions of both ions over a concentration range of 0.01 to 1.0 mM.

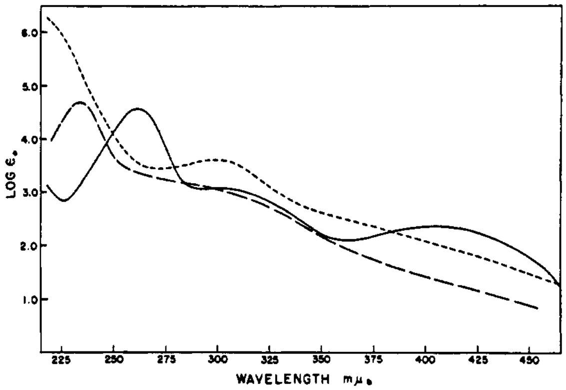

Fig. 1.—Ultraviolet absorption spectra of cobalticinium (—), rhodicinium (— —) and iridicinium (----) perchlorates in water; Beckman spectrophotometer, silica cells, 25°.

The magnetic susceptibility of rhodicinium tribromide was measured by the Gouy split tube method, using air ($\kappa = +0.029 \times 10^{-6}$ c.g.s.u.) and water (-0.72×10^{-6} c.g.s.u.) as references. The values obtained were independent of field strength. The averaged value of the molar susceptibility, χ^{25}_{mol}, is $-165 \pm 10 \times 10^{-6}$ c.g.s.u.

We are indebted to the Allied Chemical and Dye Company (Barrett Division) for financial support (F.A.C.), and to the Mallinckrodt Chemical Company (F.A.C., R.O.W.) and the Atomic Energy Commission (G.W.) for the support of research expenses.

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[3] J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952).

[4] P. L. Pauson, private communication.

Acetic Oxalic Anhydride[1]

BY W. R. EDWARDS, JR., AND WALTER M. HENLEY[2]

RECEIVED JANUARY 20, 1953

The moderate stabilities of the mixed anhydrides of oxalic acid and certain nitrobenzoic acids,[3] and of formic acetic anhydride,[4] together with the chemical behavior of the last-named, suggested that acetic oxalic anhydride (I) might be prepared and might prove useful for the synthesis of oxalic acid derivatives. Furthermore, we wished to ascertain whether it would form amides and esters of acetic acid or of oxalic acid. As its structure is in some ways unique, such preference would be of theoretical interest.

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[1] Presented before the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December 4–6, 1952.

[2] From Part 1 of the Ph.D. thesis of Walter M. Henley, Louisiana State University, August, 1952.

[3] R. Adams, W. V. Wirth and H. E. French, THIS JOURNAL, **40**, 424 (1918); R. Adams and L. H. Ulich, *ibid.*, **42**, 599 (1920).

[4] A. Behal, *Compt. rend.*, **128**, 1460 (1899).

The closest approach to a successful preparation was achieved by treating silver oxalate with acetyl chloride, in ether, at temperatures of −5° or lower; separating the ethereal solution and removing its relatively volatile components by application of reduced pressure at the same low temperature. A colorless crystalline solid was obtained. Because of its method of preparation, its hydrolysis products, its thermal decomposition products, and its reaction with aniline, this was believed to be crude (I).

When not used immediately, it was stored at −19°. In ethereal solution, it decomposed with visible evolution of gases at −3.5°, and with increasing rapidity at higher temperatures; free from solvent, it was even less stable. Feasible purification and analytical techniques were therefore limited. Even in a low-temperature room, samples of the solid material could not be weighed accurately. It was more satisfactory to employ it in ether and to estimate its concentration by treating samples with standard alkali at temperatures low enough to discourage thermal decomposition, subsequently determining the quantities of acetate and oxalate thus formed. Its reagent use appears to be confined to those few reactions which occur readily in cold systems.

Attempts to prepare (I) from sodium oxalate and acetyl chloride were unsuccessful. Action of ketene on anhydrous oxalic acid gave what appeared to be a slightly higher yield of (I), but this method was slow and contamination of the product was probably greater. Direct action of acetic anhydride on anhydrous oxalic acid over a wide temperature range was uniformly unsuccessful; at low temperatures, little or no reaction resulted, while at higher temperatures the familiar decomposition of oxalic acid to oxides of carbon was complete.

Hydrolysis of ethereal solutions of (I) by gradual addition of water at low temperatures yielded oxalic and acetic acids. The acetyl:oxalyl ratio, determined by low-temperature alkaline hydrolysis, averaged 2.27, compared to the theoretical value of 2. A high value for this ratio was to be expected, since partial disproportionation of (I) before or during hydrolysis would be followed by immediate decomposition of the hypothetical oxalic anhydride.

When a cold ethereal solution of (I) was treated with aniline in 1:2 molar proportions, oxanilide was formed exclusively and almost quantitatively in one instance; in another, it was the principal product, accompanied by a small amount of an oily by-product which may have contained a little acetanilide. With an excess of aniline, good yields of both oxanilide and acetanilide were obtained.

Such priority of formation of oxanilide over acetanilide is in accord with theory. Three possible influences may affect anilide formation by this anhydride: (a) the hyperconjugative effect of the methyl groups, diminishing the electrophilic character of the acetocarbonyl carbons; (b) the inductive effect of the methyl groups, exerting a similar influence; and (c) the inductive effect (electron-withdrawing in this case) of each oxalo carbonyl group on the other one, increasing the electrophilic character of the oxalocarbonyl carbons. All three effects work in the same direction, enhancing the relative electrophilic character of the oxalo carbonyl carbons as compared to the aceto ones. Oxanilide should be formed, therefore, in preference to acetanilide.

Attempts to form oxalates from (I) by treating it with various alcohols at temperatures ranging from −30 to 25° were unsuccessful, probably because of an inescapable dilemma. At very low temperatures, (I) may have formed oxalates more rapidly than acetates, but both esterification rates were negligibly low. At higher temperatures (possibly at lower ones also) disproportionation of (I) with subsequent destruction of the oxalic fragment appeared to be faster than esterification, making acetic anhydride, rather than (I), the available esterifying agent. Unless a set of conditions can be discovered in which rate of esterification exceeds rate of disproportionation by a substantial margin, it seems impossible to determine the relative priorities of oxalate and acetate formation from (I).

A mixture obtained by treating (I) with furfuryl alcohol exploded when distilled at reduced pressure.[5]

Whitford[6] explained the decomposition of anhydrous oxalic acid by acetic anhydride by proposing and offering evidence of the formation of an intermediate which decomposed readily to liberate acetic acid, carbon dioxide and carbon monoxide. He believed this intermediate to be a molecular compound, $(COOH)_2{\cdot}(CH_3CO)_2O$. Since the present work indicates that (I) can exist, and that it decomposes rapidly at temperatures at which acetic anhydride causes oxalic acid decomposition, it appears possible that the actual intermediate is acetic oxalic anhydride.

Experimental

Acetic Oxalic Anhydride.—A three-neck flask was fitted with stirrer, dropping funnel and drying tubes, shielded from light, and immersed in an ice–salt mixture in a dewar flask, maintaining a temperature of −7 to −3° during the preparation. Powdered silver oxalate (39 g. or 0.13 mole) and 200 ml. of dry ether were placed in the flask, stirring was begun, and a solution of 19 ml. (0.26 mole) of acetyl chloride in 50 ml. of dry ether was added gradually over a two-hour period. The mixture was allowed to stand overnight at a temperature of −5°. The ethereal layer was siphoned into a distilling flask maintained at −10 to −5° and subjected to a pressure of 3 to 5 mm. until apparent distillation ceased and for one additional hour. The residue, a colorless crystalline solid was stored at −19° or lower when not used immediately. Assuming it to be (I), the yield approximated 9%.

Variations of reaction and distillation temperatures between −5 and −25°, and small variations in the proportions of the reagents, using similar or longer times for the distillation of volatile matter, led to no conspicuous differences in the results.

A sharp explosion resulted when 2 ml. of acetyl chloride was added to 5 g. of powdered silver oxalate at room temperature, in the absence of any solvent.

As an alternative method, powdered anhydrous oxalic acid was suspended by stirring in ether, and treated with ketene at −17°. The ethereal solution was siphoned off and subjected to distillation at low temperature and pressure, leaving a residue similar in appearance and in chemical behavior to the product obtained from silver oxalate and acetyl chloride.

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[5] *cf.* W. R. Edwards, Jr., and L. H. Reeves, THIS JOURNAL, **64**, 1584 (1942), describing similar behavior, upon heating, of a mixture of oxalic acid and furfuryl acetate.

[6] E. L. Whitford, *ibid.*, **47**, 2934 (1925).

A sample of solid (I), allowed to come gradually to room temperature, decomposed completely, emitting a colorless gas and leaving a residue of acetic anhydride (anilide, m.p. 112.6–114°). The gas appeared to be a mixture of carbon dioxide and carbon monoxide. When it was passed through aqueous barium hydroxide, a portion of it was absorbed, forming a white precipitate which dissolved with effervescence when treated with hydrochloric acid; the remainder, unaffected by the barium hydroxide solution, burned with a blue flame.

Hydrolysis of (I).—Hydrolysis was accomplished by adding water dropwise, with stirring, to an ethereal solution of (I) at −10°, maintaining this temperature for two hours, and then allowing a slow rise to room temperature. Products were identified as acetic and oxalic acids.

Determination of Acetyl–Oxalyl Ratio.—A measured quantity of a 0.17 *N* solution of potassium hydroxide in 1:1 ethanol-water was cooled to −19° and added at the rate of one drop every five seconds, with stirring, to an ethereal solution of (I) at the same temperature. The mixture was allowed to stand for 18 hours at −19° and then for 2 hours at 3°. Total acid was determined by acidimetric titration of the excess base, oxalyl content by oxidimetric titration, and acetyl content by difference. Theoretical ratio of acetyl to oxalyl, 2.00; found, 2.23, 2.31.

Reaction with Aniline.—The concentration of (I) in an ethereal solution was estimated by the procedure just described. To a measured sample of this solution at −19° was added an ethereal solution of aniline at the same temperature, in the ratio of two moles of aniline to one mole of (I), at a rate of one drop per 10–15 seconds. The reactants then stood for 12 hours at −19°, followed by six hours at 3°. The precipitate was filtered, washed successively with ether and water, and dried under vacuum. It melted at 247.5–249°; its mixed melting point with a known sample of oxanilide was the same. It was further identified by nitrogen determination.[7]

Anal. Calcd. for $C_{14}H_{12}O_2N_2$: N, 11.66. Found: N, 11.47, 11.41.

Yield of oxanilide was theoretical in one run, 81% in another. No acetanilide was isolated, but in the second run there was a small amount of an unidentified oily by-product.

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[7] Method of I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 173.

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Cyanomethylation of Indole with Diethylaminoacetonitrile

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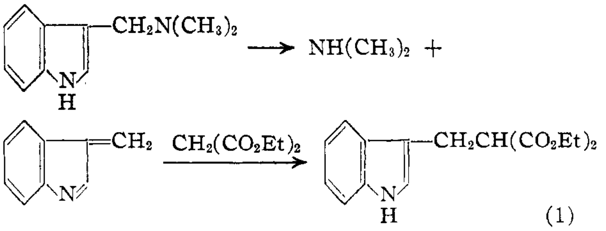
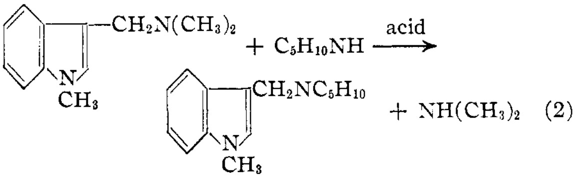
RECEIVED FEBRUARY 7, 1953

The extensive use of tertiary amines as alkylating agents[1] has prompted speculation on the mechanism of the alkylation reaction. It was at first assumed that alkylation proceeded by an elimination–addition mechanism[2] as illustrated for gramine in equation (1). Later, instances were found, however, where alkylations could not readily be explained by an elimination–addition mechanism, such as in the reaction of piperidine with 1-methylgramine[3] (equation 2) and with N-(2-nitroisobutyl)-dimethylamine,[4] and of indole[5] and diethyl malonate[6] with the Mannich base of formamidomalonic ester.





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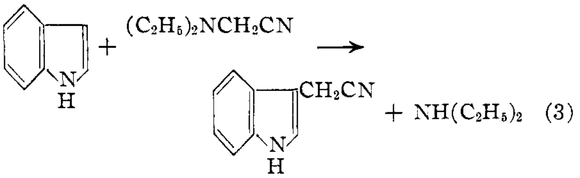

(3)

To these interesting examples of direct alkylation with tertiary amines should now be added the alkylation of indole with diethylaminoacetonitrile (equation 3). This alkylation proceeds at *ca.* 170° in the absence of a solvent to produce indole-3-acetonitrile in moderate (33–44%) yield. The nitrile was identified by comparison of its infrared spectrum with that of an authentic sample,[7] by the melting point of its picrate[7] and by hydrolysis to the acid in excellent yield. This identification incidentally indicates that the nitrile obtained by the "cyanomethylation" reaction was a very pure sample, and that the method here developed is a convenient one for the preparation of indole-3-acetonitrile on a small scale. Unfortunately attempts to scale up the preparation resulted in diminishing yields; this is probably due to the great sensitivity of the cyanomethylation reaction to temperature fluctuations. At temperatures below 160° very little reaction ensues at all, while around 180° tar formation supervenes.

While this work was in progress, a publication appeared[6] describing unsuccessful attempts at alkylating diethyl formamidomalonate with diethylaminoacetonitrile and piperidinoacetonitrile. We were likewise unable to alkylate acetophenone, 2-naphthyl methyl ether or 2-naphthol with diethylaminoacetonitrile; in the former two cases the starting materials were recovered while in the latter case phenolic polymers constituted the bulk of the reaction product.

Experimental

Indole-3-acetonitrile.—A mixture of 11.8 g. (0.1 mole) of indole[8] and 22.4 g. (0.2 mole) of diethylaminoacetonitrile[9]

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[1] For a review, see J. H. Brewster and E. L. Eliel in R. Adams "Organic Reactions," Vol. 7, John Wiley and Sons, Inc., New York, N. Y., 1953, chapter 3.

[2] K. Auwers, *Ber.*, **36**, 1878 (1903); *Ann.*, **344**, 131 (1906); K. von Auwers and Ph. Bullmann, *Ber.*, **59**, 2719 (1926); C. Mannich, W. Koch and F. Borkowsky, *ibid.*, **70**, 355 (1937); H. R. Snyder and E. L. Eliel, THIS JOURNAL, **70**, 1703 (1948); H. R. Snyder and J. H. Brewster, *ibid.*, **70**, 4230 (1948); C. E. Dalgliesh, *ibid.*, **71**, 1697 (1949).

[3] H. R. Snyder and E. L. Eliel, *ibid.*, **70**, 4233 (1948).

[4] H. R. Snyder and W. E. Hamlin, *ibid.*, **72**, 5082 (1950).

[5] A. Butenandt, H. Hellmann and E. Renz, *Z. physiol. Chem.*, **284**, 175 (1949).

[6] H. Hellmann and E. Brendle, *ibid.*, **287**, 235 (1951).

[7] J. Thesing and F. Schülde, *Ber.*, **85**, 324 (1952).

[8] We are indebted to E. I. du Pont de Nemours and Co., Inc., for a generous gift of indole.

[9] C. F. H. Allen and J. A. VanAllan, *Org. Syntheses*, **27**, 20 (1947).