Additional evidence for reaction 1 is that the $E_{1/2}$ corresponds closely to those of chloral hydrate[3a] and trichloroacetaldehyde diethyl acetal[3b] which are similar in structure to trichloroethanol. Runs in 0.1 *M* tetra-*n*-butylammonium iodide in 67% methanol–water showed only one wave of $E_{1/2}$ of −1.67 v. over the potential range of 0 to −2.5 v. *vs.* S.C.E. Dichloro- and chloroethanol are probably reduced at more negative potentials.

Acidic Nature of Trichloroethanol.—Ethanol in aqueous solutions behaves as an extremely weak acid; trichloroethanol, by analogy with the chloroacetic acids, would be expected to be a much stronger acid. The $E_{1/2}$ values (Fig. 1) seem to be independent of *p*H in a given buffer system up to *p*H 10 or 11; at higher *p*H, $E_{1/2}$ shifts to more negative potentials. Accurate $E_{1/2}$ values could not be determined at *p*H higher than 12.4 due to interference from background discharge. Presumably, if values in the higher *p*H region were known, an S-type $E_{1/2}$ *vs.* *p*H curve would be obtained.

Such S-shaped relations between *p*H and $E_{1/2}$ have been observed for a variety of acidic compounds, *e.g.*, unsaturated acids,[4] 2-haloalkanoic acids,[2,5] iodobenzoic acids,[6] iodophenols[6] and nitrophenol.[7] Tachi[8] determined the pK_a of neutral red and benzoylacetone from such a relation. The interpretation of this relationship is discussed by Saito,[5a] Tanford and Wawzonek,[9] and Elving and Rosenthal.[4b]

Experimental

Chemicals.—Stock alcoholic solutions (10.0 millimolar) were prepared from a redistilled research sample of 2,2,2-trichloroethanol (Westvaco Chemical Division of the Food Machinery Corp.), b.p. 55° at 15 mm., $n^{25}D$ 1.4852 (lit. b.p. 58–60° at 16 mm.), and Eastman Kodak Co. white label grade ethylene chlorohydrin. Nitrogen used for deoxygenating was purified and equilibrated by bubbling through sulfuric acid an alkaline pyrogallol solution, water and a portion of the test solution. Buffer solutions (Table I) were prepared from C.P. chemicals.

Apparatus.—A Leeds and Northrup Type E Electro-Chemograph was used for all polarographic and potential measurements. A Beckman model G *p*H meter was used for *p*H measurement. All measuring apparatus was calibrated. A thermostated H-cell[10] employing a saturated calomel reference electrode was used. The dropping mercury electrode, prepared from Corning marine barometer tubing, had *m* and *t* values (open circuit, distilled water, 25°, 60 cm. head) of 0.916 mg./sec. and 5.6 sec. Coulometric runs were made in a modified Lingane apparatus[11] maintained at 25 ± 0.1°.

TABLE I

BUFFER SOLUTIONS

Buffer	*p*H	Composition
1	2.2	0.5 *M* KCl with added HCl
2	4.9	0.5 *M* NaOAc with added HOAc
3	6.0	0.126 *M* $Na_2HPO_4 \cdot 12\ H_2O$, 0.0368 *M* citric acid monohydrate and 0.156 *M* KCl
	7.0	0.164 *M* $Na_2HPO_4 \cdot 12\ H_2O$, 0.0176 *M* citric acid monohydrate, and 0.073 *M* KCl
	8.0	0.194 *M* $Na_2HPO_4 \cdot 12\ H_2O$, 0.0028 *M* citric acid monohydrate
4	8.3–9.6	0.5 *M* NH_4Cl with added NH_3
5	9.2	0.082 *M* $Na_2B_4O_7 \cdot 10\ H_2O$ and 0.320 *M* KCl
	9.5	0.082 *M* $Na_2B_4O_7 \cdot 10\ H_2O$, 0.302 *M* KCl, with added NaOH
	9.8	0.082 *M* $Na_2B_4O_7 \cdot 10\ H_2O$, 0.285 *M* KCl, with added NaOH
6	10.3	0.163 *M* $Na_2HPO_4 \cdot 12\ H_2O$ with added NaOH
	11.5	0.145 *M* $Na_2HPO_4 \cdot 12\ H_2O$ with added NaOH
	12.4	0.105 *M* $Na_2HPO_4 \cdot 12\ H_2O$ with added NaOH
7	11.1–12.3	0.5 *M* KCl with added NaOH

Procedure.—The test solutions (ionic strength of 0.45), prepared by mixing measured volumes of stock and buffer solutions, had essentially the same *p*H as the buffer used. The test solution was deoxygenated and then electrolyzed; the nitrogen atmosphere was maintained throughout the electrolysis.

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[3] (a) Philip J. Elving and C. Eugene Bennett, *J. Electrochem. Soc.*, accepted for publication; (b) P. Federlin, *Compt. rend.*, **232**, 60 (1951).

[4] (a) P. J. Elving and C. Teitelbaum, THIS JOURNAL, **71**, 3916 (1949); (b) P. J. Elving and I. Rosenthal. *Anal. Chem.*, accepted for publication.

[5] (a) E. Saito, *Bull. soc. chim. France*, 404 (1948); (b) P. J. Elving and C.-S. Tang, THIS JOURNAL, **72**, 3244 (1950); (c) **74**, 6109 (1952); (d) P. J. Elving, I. Rosenthal and M. K. Kramer, *ibid.*, **73**, 1717 (1951); (e) I. Rosenthal, C.-S. Tang and P. J. Elving, *ibid.*, **74**, 6112 (1952); (f) I. Rosenthal, C. H. Albright and P. J. Elving, *J. Electrochem. Soc.*, **99**, 227 (1952); (g) P. J. Elving, J. M. Markowitz and I. Rosenthal, *ibid.*, **101**, 195 (1954).

[6] E. Gergely and T. Iredale, *J. Chem. Soc.*, 3502 (1951).

[7] M. Shikata and M. Watanabe, *J. Agr. Chem. Soc. Jap.*, **4**, 924 (1928).

[8] I. Tachi, *Mem. Coll. Agr., Kyoto Imp. Univ.*, No. **42**, Ser. No. 22, 65 (1938).

[9] C. Tanford and S. Wawzonek. *Ann. Rev. Phys. Chem.*, **3**, 247 (1952).

[10] J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

[11] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

By-product from the Osmium Tetroxide Hydroxylation of 20-Cyano-17-pregnene-21-ol-3,11-dione 21-Acetate

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Hydrolytic cleavage of the osmium tetroxide complex (II), obtained as an intermediate in the hydroxylation of 20-cyano-17-pregnene-21-ol-3,11-dione 21-acetate (I)[1] yields predominantly IIIa together with varying amounts of a by-product. This by-product was found to be a nitrogen-containing substance giving a strong test for cyanide and possessing two acetate functions as measured by acetyl group determination. The by-product rapidly reduced Tollens reagent, gave a positive Porter–Silber test,[2] and otherwise exhibited normal characteristics for the 17-hydroxy cortical side-chain. This substance, however, failed to give a dinitrophenylhydrazone derivative at room temperature under conditions whereby IIIa rapidly derivatized; pregnane-3α,17α,21-triol-11,20-dione 3,21-diacetate also did not derivatize under similar

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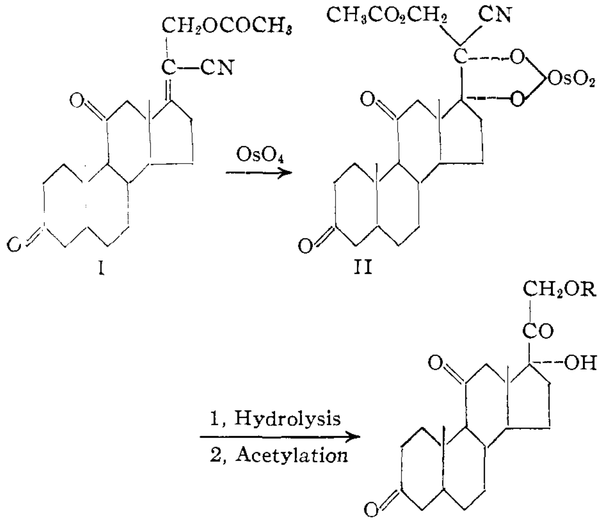
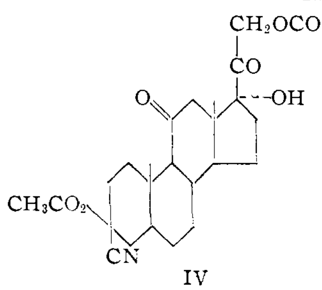
[1] L. H. Sarett, THIS JOURNAL, **70**, 1454 (1948).

[2] C. C. Porter and R. H. Silber, *J. Biol. Chem.*, **185**, 201 (1950).



III, R = H
IIIa, R = CH₃CO



IV

conditions. This observation made it virtually certain that the 3-keto group of the by-product was masked in the form of a cyanohydrin acetate and could be represented by structure IV. This structure was confirmed by submitting the by-product to hot bicarbonate hydrolysis whereby it was converted to III. The formation of IV during the decomposition of the osmium complex II is an interesting example of hydrogen cyanide transfer within a polycarbonyl system.

Experimental

By-product (IV).—Isolated by chromatography of the mother liquors obtained from the crystallization of IIIa; microprisms from methanol m.p. 226.5–228.5°; infrared $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.83 μ (-OH), 5.73 μ (-OAc) and 5.85 μ (C=O).

Anal. Calcd. for $C_{26}H_{35}O_7N$: C, 65.94; H, 7.45; N, 2.96; CH_3CO, 18.2. Found: C, 66.13; H, 7.46; N, 2.88; CH_3CO, 18.9.

Treatment of IV in methanol with 2,4-dinitrophenylhydrazine reagent[3] at room temperature failed to give a derivative.

Hydrolysis of By-product (IV).—A suspension of 15 g. of the by-product IV in 380 cc. of methanol and 190 cc. of 1 *N* aqueous potassium bicarbonate was refluxed for 30 minutes. During this period the reaction mixture became homogeneous. The methanol was evaporated *in vacuo* at 35° and the product extracted with ethyl acetate. The ethyl acetate extracts were combined, washed with water, dried over anhydrous sodium sulfate and concentrated to dryness to give 11.1 g. of crude III. Recrystallization from acetone gave a first crop of 5.98 g. of III, m.p. 225–228°, not depressed on admixture with authentic III. **Acetate IIIa** obtained by the acetylation of the hydrolyzed by-product with acetic anhydride in pyridine melted at 226.5–230° and showed no depression on admixture with authentic IIIa; the infrared spectrum was identical with an authentic specimen of IIIa.

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[3] R. C. Fuson and R. L. Shriner, "The Systematic Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

Anthochlor Pigments. IX. The Structure of the Aurone Pigment of *Cosmos sulfureus*, "Orange Flare" and "Yellow Flare"

BY T. A. GEISSMAN AND LEONARD JURD

RECEIVED APRIL 20, 1954

Nordström and Swain[1] recently observed that synthetic 6,3′,4′-trihydroxyaurone[2] (I) appeared to be different from sulfuretin, the aurone pigment isolated from *Cosmos sulfureus* by Shimokoriyama and Hattori and assigned the structure I.[3] Our own observations on the pigments of the orange and yellow color forms of *C. sulfureus* had found us in complete agreement with the conclusion of Shimokoriyama and Hattori as to the structure of sulfuretin, since (a) the absorption spectrum (Fig. 1) of sulfurein (II) (sulfuretin glucoside) is very similar to that of leptosin (III); (b) the co-occurrence[3] of coreopsin and sulfurein (see Fig. 1) suggests a biogenetic relationship paralleling that existing between leptosin and lanceolin in *Coreopsis grandiflora*[3] and *Coreopsis lanceolata*[3]; (c) the purple color given by sulfurein in alkali is virtually identical with that given by leptosin; and (d) the R_f values of sulfurein and sulfuretin on paper chromatograms are entirely consistent with the structures I and II.

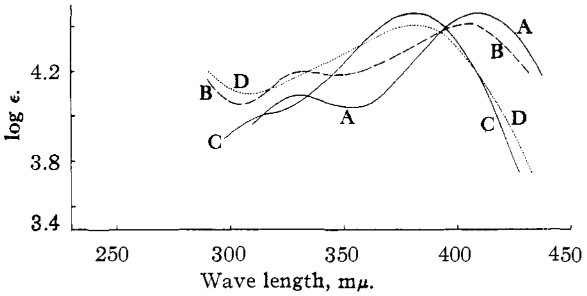
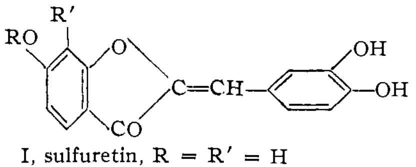


Fig. 1.—Absorption spectra (in EtOH) of: A, leptosin; B, R_f 0.66 component of *Cosmos sulfureus;* C, butein; D, R_f 0.71 component of *Cosmos sulfureus*. R_f values are for butanol–acetic acid–water, on Whatman No. 1 paper.

The report of Nordström and Swain that the triacetate of synthetic I has a m.p. about 25° lower than sulfuretin acetate[3] suggested that sulfuretin was actually different from I or that the substance isolated from *C. sulfureus* was not a pure compound.



I, sulfuretin, R = R′ = H
II, sulfurein, R = glucosyl; R′ = H
III, leptosin, R = glucosyl; R′ = OCH_3

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[1] C. G. Nordström and T. Swain, *Chemistry and Industry*, 823 (1953).

[2] E. C. Bate-Smith and T. A. Geissman, *Nature*, **167**, 688 (1951).

[3] M. Shimokoriyama and S. Hattori, THIS JOURNAL, **75**, 1900 (1952).