peak volumes essentially the same as those observed previously.[8] The observed, total yields of acids, corrected for an established slight loss on the silicic acid columns, were 28 meq. of lactic acid, 1.6 meq. of formic acid, 0.8 meq. of acetic acid and 6.0 meq. (by difference) of other acids from the reaction with sodium hydroxide; and 12 meq. of lactic acid, 5.8 meq. of formic acid, 1.5 meq. of acetic acid and 20 meq. (by difference) of other acids from the reaction with calcium hydroxide.

Radioassay of Derivatives.—The separated samples of formic acid were converted to benzimidazole; those of acetic acid to 2-methylbenzimidazole and benzimidazole; and those of lactic acid to 2-(α-hydroxyethyl)-benzimidazole, benzimidazole-2-carboxylic acid and benzimidazole as described previously.[8,10] All purified samples for radioassay showed melting points in agreement with reported values. Radioassay data[17] for the various derivatives are shown in Table **I**.

"α"-D-Glucosaccharinic Lactone.—After elution from the silicic acid column of the acetic, formic and lactic acids produced in the reaction with calcium hydroxide (20% aliquot) with 1-butanol-chloroform,[8] the column was further developed with benzene-methanol (8:1, v./v.). A fraction of acidic material, containing sulfuric acid from the preconditioning of the column and organic acids, was obtained at a peak volume of 175 ml. Sulfate was precipitated from this fraction with barium hydroxide and barium ions then were removed from the filtered solution by ion-exchange. Concentration yielded a light-colored sirup which was seeded with "α"-D-glucosaccharinic lactone. After several months, the crystals that had formed were separated on a porous clay plate and recrystallized from water. The product (*ca.* 30 mg.) showed the correct properties for "α"-D-glucosaccharinic lactone: m.p. 160–162°, $[\alpha]^{25}D$ 92° in water, *c* 0.5; quinine salt,[20] m.p. 140–142° and $[\alpha]^{25}D$ −114° in water, *c* 0.5. Radioactivity of the lactone was approximately 4 × 10^5 cts./min./mM.

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(20) Nef[5] reports m.p. 152° for this salt. H. Kiliani and P. Loeffler, *Ber.*, **37**, 1196 (1904), record m.p. 141–142°, and H. Kiliani, P. Loeffler and O. Matthes, *ibid.*, **40**, 2999 (1907), record $[\alpha]D$ −102.6° in water. Prepared in this Laboratory from known "α"-D-glucosaccharinic lactone (obtained by the alkaline isomerization of D-mannose[8]) and recrystallized several times from water–acetone, the salt showed m.p. 141–142° and $[\alpha]^{28}D$ −115° in water, *c* 0.6.

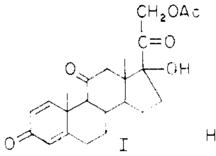
ST. LOUIS 5, MISSOURI

COMMUNICATIONS TO THE EDITOR

THE PHOTOCHEMISTRY OF PREDNISONE ACETATE IN NEUTRAL SOLUTION

Sir:

We recently reported[1] that the medicinally important[2] prednisone acetate (I) was converted on irradiation in refluxing aqueous acetic acid into II. Such a rearrangement reaction has been well exemplified.[3] In neutral solution analogy with the photochemistry of santonin[4] would suggest that products of a different type would be formed. We now wish to report that irradiation of I with ultraviolet light in ethanol solution affords lumiprednisone acetate (III), m.p. 224–226°, $[\alpha]D$ −84° (*c* 0.80; all rotations in $CHCl_3$), $\lambda\lambda_{max}$ 218 and 265 mμ (ε 5,900 and 2,300, respectively; all ε in EtOH), infrared max. (all max. in $CHCl_3$) at 1735 (21 acetate), 1708 (11 and 20 ketones), 1690 (conjugated ketone) and 1575 (conjugated C=C) cm.$^{-1}$; calcd. for $C_{23}H_{28}O_6$: C, 69.0; H, 7.05; 3 C–Me (1 from the 21 OAc), 11.3. Found: C, 68.95; H, 7.05; C–Me, 9.5%. The spectra are typical of an umbellulone.[4,5] Palladized charcoal hydrogenation of III gives a saturated dihydro-derivative IV, m.p. 200–203°, $[\alpha]D$ +95° (*c* 1.15), λ_{max} 207 mμ (ε 8,100); expected infrared max.; calcd. for $C_{23}H_{30}O_6$: C, 68.6; H, 7.5. Found: C, 68.8; H, 7.65. The ultraviolet spectrum coupled with stability to ozone show the presence of conjugated ketone and cyclopropane groups.[4,5] Treatment of III with 0.2% $HClO_4$ in acetic acid at 85° for 20 minutes affords an isomer V, m.p. 202–204°, $[\alpha]D$ −103° (*c* 0.50), λ_{max} 241 mμ (ε 10,600), expected infrared max.; found: C, 68.8; H, 6.85; C–Me, 11.9%. Hydrogenation over palladized charcoal gives a dihydro-derivative VI, m.p. 192–195°, $[\alpha]D$ +127° (*c* 0.50), λ_{max} 251 mμ (ε 8,700), expected infrared max.; found: C, 68.6; H, 7.35; also obtained from IV by isomerization over alumina (Brockmann[6] Grade III). The ultraviolet subtraction curve of VI from V gave λ_{max} 219 mμ (ε 7,300) in a good agreement[4,7] with that expected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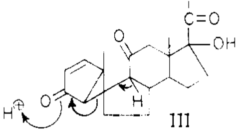
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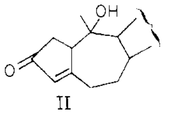
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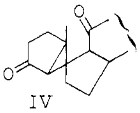
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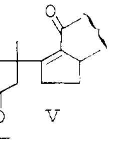
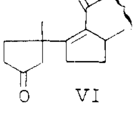

V


VI

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(1) D. H. R. Barton and W. C. Taylor, *Proc. Chem. Soc.*, 147 (1957).

(2) H. L. Herzog, C. C. Payne, M. A. Jevnik, D. Gould, E. L. Shapiro, E. P. Oliveto and E. B. Hershberg, THIS JOURNAL, **77**, 4781 (1955); A. Nobile, W. Charney, P. L. Perlman, H. L. Herzog, C. C. Payne, M. E. Tully, M. A. Jevnik and E. B. Hershberg, *ibid.*, **77**, 4184 (1955)

(3) D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 929 (1957); D. H. R. Barton and J. E. D. Levisalles, unpublished observations.

(4) D. H. R. Barton, P. de Mayo and M. Shafiq, *Proc. Chem. Soc.*, 205 (1957); *J. Chem. Soc.*, in press; D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957); see also W. Cocker, K. Crowley, J. T. Edward, T. B. H. McMurry and R. T. Stuart, *J. Chem. Soc.*, 3416 (1957).

(5) R. H. Eastman, THIS JOURNAL, **76**, 4115 (1954); and refs. there cited.

(6) H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941).

(7) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 (1942); A. E. Gillam and T. F. West, *J. Chem. Soc.*, 486 (1942).

for an unsubstituted cyclopentenone. Wolff–Kishner reduction of VI followed by chromic acid oxidation of the product in a current of steam[8] gave acetic acid and 1-methylcyclopentanecarboxylic acid.[9]

The appropriate blank experiments showed that only the chromophore of ring A of I was involved in photochemical change. As expected[4] III was stable to hot aqueous acetic acid and is *not* the precursor of II. It is possibly analogous to the "compound A4" obtained recently[10] by irradiation of 1-dehydrotestosterone acetate.

[8] F. Pregl, "Quantitative Organic Microanalysis," Ed. J. Grant, J. and A. Churchill, London, 5th edition, 1951, p. 206.

[9] H. Meerwein, *Ann.*, **417**, 255 (1918).

[10] H. Dutler, H. Bosshard and O. Jeger, *Helv. Chim. Acta*, **40**, 494 (1957).

[11] Arthur D. Little, Visiting Professor, Massachusetts Institute of Technology, Cambridge, Mass., 1958.

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RECEIVED NOVEMBER 25, 1957

COPPER SALT CATALYSIS OF THE AIR OXIDATION OF REDUCED URANIUM COMPOUNDS IN CARBONATE-BICARBONATE SOLUTIONS[1]

Sir:

Recent increasing interest in the carbonate leaching of uranium ores[2] prompts us to report the following data.

We have found that copper salts, especially in the presence of ammonia, catalyze the air oxidation and dissolution of reduced uranium compounds in carbonate–bicarbonate solutions.

The rate of U_3O_8 dissolution in air-blown 0.5 *M* Na_2CO_3–0.5 *M* $NaHCO_3$ was increased by a factor of approximately seven in the presence of 25 mg. copper/l. (added as copper sulfate) and by a factor of 14 when 0.1 *M* NH_4OH was also present. When the copper sulfate was added to the 0.5 *M* Na_2CO_3–0.5 *M* Na HCO_3 solution, no precipitate formed, but the solution acquired a blue color more intense than can be accounted for on the basis of a simple cupric species. This suggests the formation of a cupric carbonato complex.[3] The addition of ammonia intensified the color further indicating a change in the cupric species present. The rate of UO_2 dissolution was increased only slightly by the presence of copper salts alone but was increased by a factor of over two in the presence of copper salts and ammonia. The U_3O_8 for these experiments was prepared by decomposition at 1100° of UO_3 obtained from the S. W. Shattuck Co. The UO_2 was obtained from them as such.

A brief study was made to determine the factors involved in the rate of the copper-catalyzed U_3O_8 dissolution. Since dissolution at 90° is over three times faster than at 70° all of the following results were determined at 90°. The initial rate is directly proportional to the surface area of the U_3O_8 added. Neither ionic strength nor total CO_2, at constant *p*H, has any effect. The use of oxygen instead of air has no effect beyond that due to the increase in the rate of uncatalyzed air oxidation. The use of nitrogen instead of air decreases the rate by a factor of over 2.5. (Sufficient copper salt was used so that the decrease in cupric copper concentration was not significant.) This indicates that in the air blown system an oxidizing species other than cupric copper is formed in the catalytic process. The most likely compound is hydrogen peroxide from the reduction of oxygen during the air oxidation of the reduced copper substance. Part of the U_3O_8 is presumably oxidized by this hydrogen peroxide.

The dependence on copper concentration is approximately first power under nitrogen, but very low (less than 0.3 power) under air (see Fig. 1).

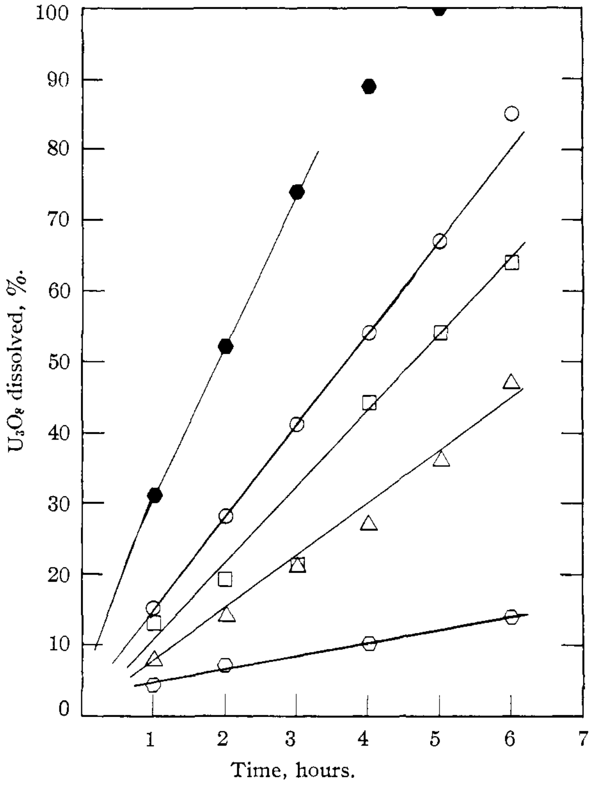

Fig. 1.—Dissolution of 1 g./l. U_3O_8 in air-blown 0.5 *M* Na_2CO_3 at 90°: ●, 25 mg./l. Cu, 0.1 *M* NH_4OH; ○, 25 mg./l. Cu; □, 2.5 mg./l. Cu; △, 0.25 mg./l. Cu; ⊖, no Cu.

The effects of the variables on the rate of U_3O_8 dissolution in the presence of copper and ammonia are qualitatively similar to those with copper alone.

Cobalt, manganese, thallium and vanadate salts have also been shown to act as catalysts, but they are not as effective as copper salts.

WESTERN DIVISION
ARTHUR D. LITTLE, INC. WARREN E. CLIFFORD
SAN FRANCISCO, CALIFORNIA

RECEIVED OCTOBER 14, 1957

[1] This work was carried out for the Atomic Energy Commission under Contract AT(49-6)-923.

[2] R. G. Beverly, A. W. Griffith and W. A. Millsap, *Mining Engineering*, **9**, 988 (1957).

[3] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, England, 1950, p. 168.

A NEW SYNTHESIS OF TROPOLONE

Sir:

A new synthesis of tropolone starting from tetrafluoroethylene and cyclopentadiene has been discovered. The key to this synthesis is the thermal