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.

IMPERIAL COLLEGE
LONDON, S.W. 7 D. H. R. BARTON[11]
ENGLAND W. C. TAYLOR

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).

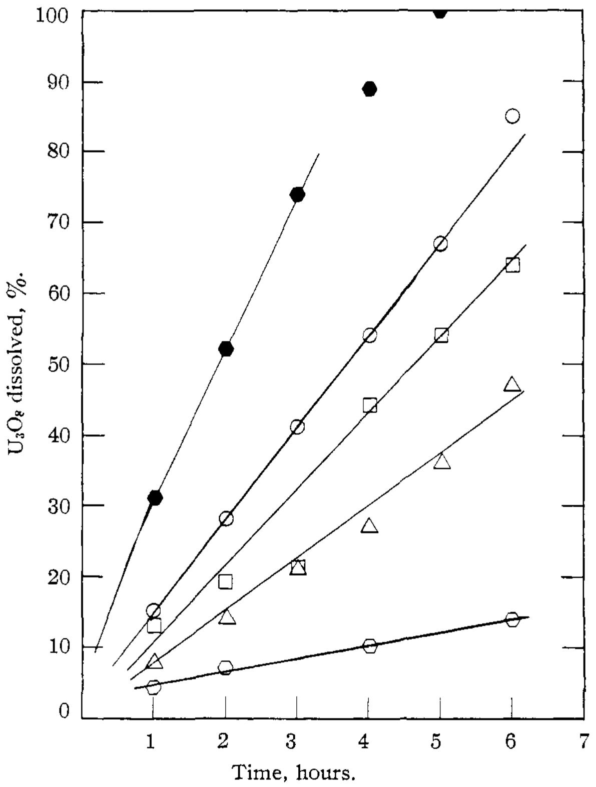


Fig. 1.—Dissolution of 1 g./l. U_3O_8 in air-blown 0.5 *M* Na_2CO_3 at 90°: ⬢, 25 mg./l. Cu, 0.1 *M* NH_4OH; ○, 25 mg./l. Cu; □, 2.5 mg./l. Cu; △, 0.25 mg./l. Cu; ⊖, no Cu.

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.

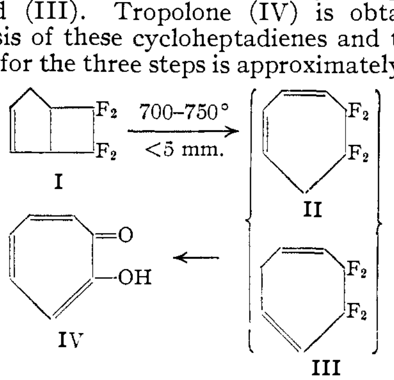
[2] R. G. Beverly, A. W. Griffith and W. A. Millsap, *Mining Engineering*, **9**, 988 (1957).

[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 rearrangement of the tetrafluoroethylene–cyclopentadiene adduct, 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene[1] (I), to tetrafluorocycloheptadienes (II) and (III). Tropolone (IV) is obtained by hydrolysis of these cycloheptadienes and the overall yield for the three steps is approximately 20%.



Thermal rearrangement of the bicycloheptene was accomplished by pyrolysis at 700–750° under pressures of less than 5 mm. The pyrolysate was fractionated, and selected fractions were further purified by gas chromatography to give *5,5,6,6-tetrafluoro-1,3-cycloheptadiene* (*II*), b.p. 63° (50 mm.), $n^{25}\text{D}$ 1.4141, λ-max 240 mμ (ϵ = 9460) (*Anal.* Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64. Found: C, 51.06; H, 4.29), and *6,6,6,7-tetrafluoro-1,4-cycloheptadiene* (III), b.p. 78° (50 mm.), $n^{25}\text{D}$ 1.4014 (*Anal.* Calcd. for $C_7H_6F_4$: C, 50.61; H, 3.64; F, 45.75; hydrogenation 0.0245 g. H_2/g. sample. Found: C, 50.95; H, 3.92; F, 45.99; hydrogenation 0.0231, 0.0232 g. H_2/g. sample). Infrared absorption and nuclear magnetic resonance spectra of these isomers confirmed the structure assignments. The combined yield of cycloheptadienes II and III was of the order of 50–65% at 50% conversion.

Hydrolysis of the mixture of tetrafluorocycloheptadienes obtained from the thermal rearrangement gave tropolone in 70% yield. The hydrolysis was accomplished by heating under reflux the cycloheptadienes in acetic acid containing potassium acetate and a small amount of water. Tropolone, m.p. 50–51°, was positively identified by comparison of its infrared spectrum with that of authentic material[2] and by conversion to the green copper chelate.

Acknowledgments.—The assistance of Drs. O. W. Webster and W. R. Brasen of This Laboratory is gratefully acknowledged.

(1) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, This Journal, **71**, 490 (1949).

(2) Prepared by Dr. E. G. Howard of This Laboratory by bromination of 1,2-cycloheptanedione.

Contribution No. 452 from the
Central Research Department
Experimental Station
E. I. du Pont de Nemours and Co.
Wilmington, Delaware

J. J. Drysdale
W. W. Gilbert
H. K. Sinclair
W. H. Sharkey

Received December 4, 1957

PHOTOREDUCTION OF TRIPHOSPHOPYRIDINE NUCLEOTIDE BY CHROMATOPHORES OF *Rhodospirillum rubrum*

Sir:

Reasoning from the knowledge gained about photosynthesis in green plants, it is thought that the primary photochemical reaction in bacterial photosynthesis is a splitting of water under the influence of light and bacterial chromatophores to produce an oxidative and a reductive system. In green plants the oxidative system is dissipated as molecular oxygen, but this is not the case with photosynthetic bacteria. Accordingly, the oxidative system so generated must be accommodated by oxidation–reduction reactions occurring in the cell. Back reaction of the oxidative system with the reductive system *via* an electron transport system maintained in the chromatophore occurs, and is linked to phosphorylation resulting in ATP formation.[1] This potential for the oxidative system to react back either directly through such an electron transport system contained in the chromatophore, or indirectly through a series of cytoplasmic reactions, probably accounts for the inability to demonstrate directly a reduction of the pyridine nucleotides with illuminated extracts of photosynthetic bacteria. Repeated experiments directed toward this goal by the author have not been successful. This is in contrast to plant chloroplasts, which can be shown to reduce both diphosphopyridine nucleotide (DPN) and triphosphopyridine nucleotide (TPN) under the influence of light, with an accumulation of the reduced forms, DPNH and TPNH.[2,3]

If pyridine nucleotides were being reduced by bacterial chromatophores and rapidly reoxidized by the oxidative system generated simultaneously, it might be possible to demonstrate such a reduction by trapping the reduced pyridine nucleotides with thermodynamically favorable enzyme systems. Such a system for TPNH would consist of oxidized glutathione and glutathione reductase, while one for DPNH would be pyruvate and lactic dehydrogenase. These systems were used earlier for demonstration of DPNH and TPNH formation by plant chloroplasts in the light.[4,5] The results of such experiments using chromatophores from *Rhodospirillum rubrum* are presented in Table I. It is possible to demonstrate TPNH formation by illuminated chromatophores by such a coupled reaction. A requirement for spinach pyridine nucleotide reductase (the enzyme from plants necessary for pyridine nucleotide reduction by illuminated chloroplasts) indicates a similar mechanism of pyridine nucleotide reduction in both plant and bacterial systems. Preliminary experiments indicate that *R. rubrum* chromatophores are much more efficient in affecting TPN photoreduction when compared with DPN. Thus, a system similar to the one listed in Table I, but substituting DPN for TPN and utilizing a pyruvate–lactic dehydrogenase system to trap DPNH formed, produced only 0.06 μmole of lactate as a function of illumination. It is significant that the photoproduction of lactate in the DPN system is stimulated by the addition of TPN, while the photo-

(1) A. W. Frenkel, *J. Biol. Chem.*, **222**, 823 (1956).

(2) A. San Pietro and H. M. Lang, *Science*, **124**, 118 (1956).

(3) D. I. Arnon, F. R. Whatley and M. B. Allen, *Nature*, **180**, 182 (1957).

(4) D. D. Hendley and E. E. Conn, *Arch. Biochem. Biophys.*, **46**, 454 (1953).

(5) W. Vishniac and S. Ochoa, *J. Biol. Chem.*, **195**, 75 (1952).