

diethanol⁹ were isolated in small amounts as by-products, the quantities increasing when the excess of aminobutanol was decreased. An interesting alternative synthesis, reductive alkylation of 2-aminobutanol with glyoxal using sodium borohydride¹⁰ as reducing agent, gave good yields.

This work has shown that in mice the dextro form of 2,2'-(ethylenediimino)-di-1-butanol is more active and less toxic than streptomycin when administered parenterally and possesses an oral efficacy index (ratio of maximum tolerated dose to median effective dose) at least equivalent to that of isoniazid. A series of papers is in preparation covering studies of numerous homologs and of various analogs and modifications of the functional groups of this chemotherapeutic agent.

(9) *meso*-Dihydrochloride, m.p. 246.5–247.5° dec. (\pm)-dihydrochloride, m.p. 238–239° dec.

(10) J. H. Billman and A. C. Diesing, *J. Org. Chem.*, **22**, 1068 (1957), used this reagent for reduction of aromatic Schiff bases.

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RECEIVED MARCH 24, 1961

A NEW PHOTOCHEMICAL PRIMARY PROCESS, THE PHOTOCHEMICAL ENOLIZATION OF *o*-SUBSTITUTED BENZOPHENONES

Sir:

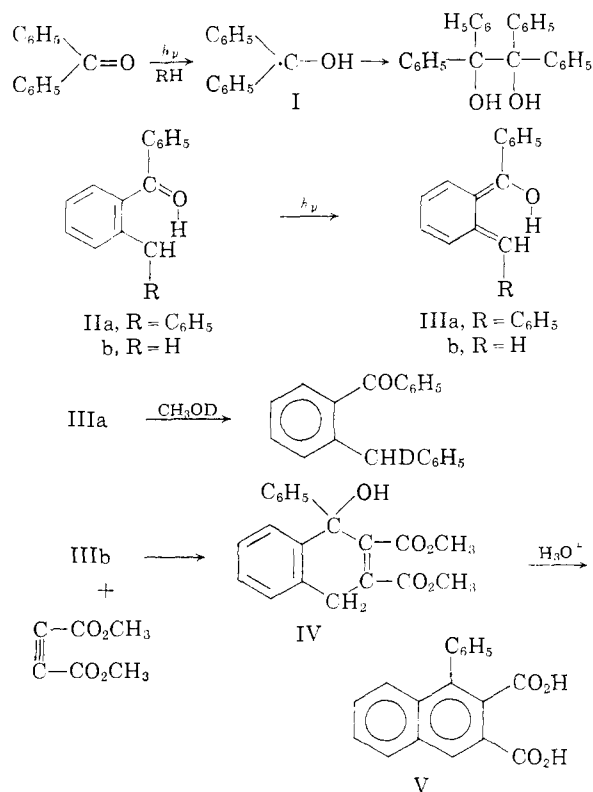
We wish to report a new type of photochemical primary process, the photochemical enolization of *o*-substituted benzophenones. Benzophenone readily is reduced photochemically in the presence of hydrogen donors to give benzopinacol *via* a ketyl radical intermediate (I).¹ Photochemical pinacol reduction is suppressed completely and no ketyl radical formation is detected if the benzophenone is substituted at the *ortho* position by an alkyl group containing an α -hydrogen. Instead, *o*-alkylbenzophenone (II) undergoes intramolecular hydrogen transfer to give the corresponding enol under the influence of ultraviolet light. Photochemical enolization of this type has been demonstrated unequivocally by these observations.

o-Benzylbenzophenone (IIa) is extremely stable toward ultraviolet radiation generated by either low pressure or high pressure mercury arcs. The compound was recovered unchanged after prolonged irradiation in alcohol solutions and no pinacol could be detected. When a solution of IIa in CH₃OD was irradiated with a Hanovia S-200 source, the recovered IIa was found to contain 1.04–1.09 atoms of deuterium per molecule,² while no deuterium incorporation took place when the same solution was allowed to stand at ordinary laboratory conditions. By n.m.r. spectrometry, all the deuterium atoms were found to be located at the benzylic position.

The photo-enol (IIIb) of *o*-methylbenzophenone (IIb) reacts smoothly with dimethyl acetylenedicarboxylate, a dienophile, to give an adduct (IV) in excellent yield. An equimolar solution of IIb

(1) C. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959), and references therein.

(2) Deuterium analysis by Dr. Josef Nemeth of Urbana, Illinois.



and dimethyl acetylenedicarboxylate (0.06 mole) in benzene was irradiated with a Hanovia S-200 source at 15–20° for 24 hours. After the solvent was removed, the residue crystallized and no appreciable amount of polymeric material was formed. The residue was recrystallized from benzene-cyclohexane to give IV in 85% yield (m.p. 112°; found: C, 71.25; H, 5.36; λ_{\max} 3500 cm⁻¹, 1720 cm⁻¹; strong ultraviolet end absorption). The structure of IV was established by its conversion to 1-phenyl-naphthalene-2,3-dicarboxylic acid (V), identical in all respects with an authentic sample.³ The quantum yield of this photochemical addition is estimated at >0.5. The generality and further applications of this reaction are being investigated.

The authors wish to thank Professor W. A. Noyes, Jr., for some valuable discussion and Mr. Richard Atkinson for his assistance in the preparation of an authentic sample of V. C. R. is indebted to the Petroleum Research Foundation for a graduate fellowship.

(3) A. Michael, *Ber.*, **39**, 1912 (1906).

(4) Alfred P. Sloan Fellow.

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RECEIVED FEBRUARY 27, 1961

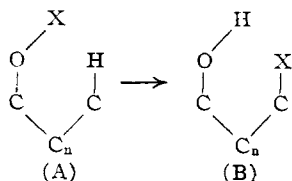
THE PHOTOCHEMICAL REARRANGEMENT OF HYPOCHLORITES

Sir:

In a recent communication¹ we adumbrated a photochemically induced rearrangement of hypochlorites of the general type (A) \rightarrow (B) (X = halo-

(1) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960).

gen). This reaction has been observed by Professor Cheves Walling² for the hypochlorites of certain aliphatic alcohols. We now wish to report two examples of the reaction in the steroid series. In both cases the chlorhydrins formed have been characterized by base treatment to give the corresponding 1,4-oxides. The photolysis of hypo-

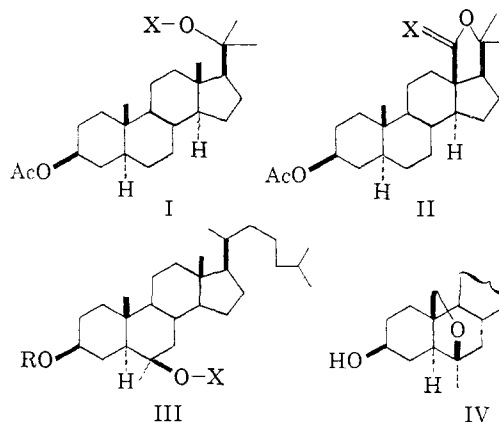


chlorites to give alkoxy radicals and atomic chlorine is, of course, well known.³

3β -Acetoxy-20-methylallopregnan-20-ol (I, X = H)⁴ was converted to the hypochlorite (I, X = Cl), m.p. 145–147°, $[\alpha]_D$ 0° (in CCl_4), $\lambda_{\text{max}}^{\text{CCl}_4}$ 258 and 318 μ ($\epsilon = 107$ and 9.5, respectively) using chlorine monoxide.⁵ This hypochlorite was photolyzed in dry benzene using a mercury lamp (200 watt, Pyrex filter)^{1,6} with water cooling. The product, refluxed with 5% methanolic potassium hydroxide for 2 hr., gave, on reacetylation and chromatography, 20-methyl-18,20-oxidoallopregnan-3 β -yl acetate (II, X = H₂) (20%), m.p. 152–154°, $[\alpha]_D$ +17° (in CHCl_3) as well as starting material (I, X = H). The constitution of the product was shown by its n.m.r. spectrum⁷ (loss of C₁₈ methyl group) and by vigorous chromic acid oxidation to the γ -lactone (II, X = O),⁸ m.p. 209–210°, $[\alpha]_D$ 0° (in CHCl_3), $\nu_{\text{max}}^{\text{KBr}}$ 1757 and 1745 cm^{-1} . The

ether (II, X = H₂) and its derived lactone (II, X = O) have been prepared independently by Cainelli, *et al.*⁸

Similarly 3β -acetoxy-6 α -methylcholestan-6 β -ol (III, R = Ac, X = H)⁹ was converted to its hypochlorite (III, R = Ac, X = Cl) and photolyzed. Base treatment of the product as above afforded 6 α -methyl-6,19-oxidocholestan-3 β -ol (IV) (50%), m.p. 179–181°, $[\alpha]_D$ +19° (in CHCl_3) as well as the diol (III, R = X = H). The constitution of (IV) was confirmed by its n.m.r. spectrum^{10,11} (loss of C₁₉ methyl group).



Acknowledgments.—We thank Dr. M. M. Pechet for his encouragement and the Misses C. Pantuck and L. Gendron for able experimental assistance.

(9) L. F. Fieser and J. Rigaudy, *J. Am. Chem. Soc.*, **73**, 4661 (1951); R. A. Sneed, *ibid.*, **80**, 3982 (1958).

(10) Satisfactory analytical data have been secured for all new compounds except that the hypochlorites were characterized through iodimetry (being thereby reduced to the parent alcohol).

(11) The substance of this Communication was given in a lecture by D. H. R. B. at the Annual General Meeting of the Chem. Soc. at Liverpool, U. K., on April 12th, 1961. At that time Dr. V. A. Petrov (B.D.H.) informed us by personal communication that he had observed similar results in steroids.

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D. H. R. BARTON

RECEIVED APRIL 19, 1961

BOOK REVIEWS

The Surface Chemistry of Metals and Semiconductors. A Symposium Sponsored by the Office of Naval Research and the Electrochemical Society, Columbus, Ohio, 1959. Edited by HARRY C. GATOS. With the assistance of J. W. FAUST, Jr., and W. J. LAFLEUR. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1960. xi + 526 pp. 16 × 23.5 cm. Price, \$12.50.

This volume is the record of a symposium on the surface chemistry of metals and semiconductors held under the auspices of the Electrochemical Society and the Office of Naval Research in October, 1959. It contains twenty-two papers which are presented in five sections entitled The Chemistry and Physics of Surfaces, Imperfections and Surface Behavior, Electrode Behavior of Metals and Semiconductors, Surface Reactions in Liquid Media, and Surface Reactions in Gaseous Media, respectively. The character

of the individual contributions varies considerably. There is, for example, a short (11 page) general introduction to the physics and chemistry of surfaces by W. H. Brattain, a report on some recent experimental investigations of oxidation-reduction reactions at the germanium electrode by H. Gerischer, and lengthy and fairly detailed review articles on the oxidation of metals by K. Haufler and by Gwathmey and Lawless.

This volume is perhaps best described as a collection of elementary review papers and, as such, should be of value to chemists and physicists seeking an introduction to recent research in the areas enumerated above. It is possible that a surface chemist or electrochemist may find some of the contributions superficial, insufficiently detailed or similar to reviews previously published in the periodical literature. However, the papers are carefully and economi-