

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

Sir:

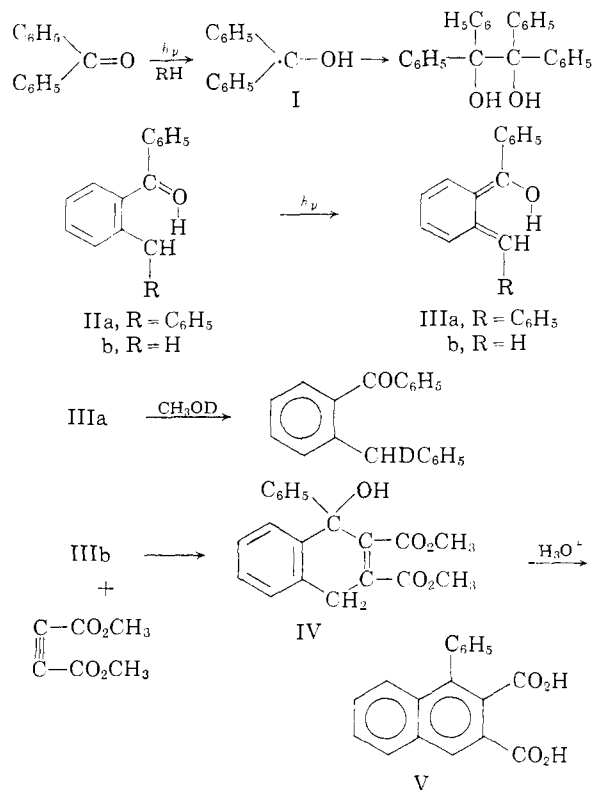
We wish to report a new type of photochemical primary process, the photochemical enolization of *o*-substituted benzophenones. Benzophenone readily is reduced photochemically in the presence of hydrogen donors to give benzopinacol *via* a ketyl radical intermediate (I).¹ Photochemical pinacol reduction 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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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).