COMMUNICATIONS TO THE EDITOR

STEREOISOMERIC *o*-HYDROXYBENZOPHENONE OXIMES

Sir:

We have found, in the extension of earlier experiments on the chemical behavior accompanying hydrogen bonding [Blatt, THIS JOURNAL, **60**, 205 (1938)], that bonded *o*-hydroxybenzophenone oximes, such as (I), readily form characteristic sparingly soluble copper derivatives, whereas stereoisomeric non-bonded oximes such as (II) do not.



The reaction is extremely sensitive, and the differentiation between stereoisomers is sharp. With the oxime (I) the limit of sensitivity is between 0.0001 g. and 0.00001 g. of oxime per cc. of solution, using an ethereal solution of the oxime and shaking with an excess of saturated aqueous copper acetate. Taking the mean of these two values, the limiting concentration of the oxime is approximately 0.0001 molar. The non-bonded isomer (II) forms no insoluble copper derivative at a concentration as high as 0.025 g. per cc., which is some five hundred-fold greater than the minimum concentration necessary with the bonded isomer. These experiments open a new approach to the problem of the structure of chelate metallic derivatives; they will be reported in detail at a later date, together with the conclusions to which they lead.

HOWARD UNIVERSITY A. H. BLATT WASHINGTON, D. C.

RECEIVED DECEMBER 16, 1938

CRYSTALLINE D-ALTROSAN¹

Sir:

Several years ago it was stated [Richtmyer and Hudson, THIS JOURNAL, 57, 1721 (1935)] that "crystalline D-altrose is converted by hot hydrochloric acid from $[\alpha]^{20}D + 34$ to -98° ; this

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

is accompanied by partial loss of reducing power, presumably due to the formation of an anhydro-D-altrose to the extent of 57% at equilibrium." At that time we attempted to isolate the assumed anhydro-altrose by oxidizing the altrose component of this equilibrium mixture (ca. 12 g.) with bromine water in the presence of barium benzoate [Hudson and Isbell, *ibid.*, **51**, 2225 (1929)], removing the benzoic acid, barium, and bromine in the customary way, and the D-altronic acid as its calcium salt; the anhydro-altrose remained and was concentrated to a sirup with the expected high levorotation. After three years in a desiccator the sirup began to crystallize, and from it has been obtained 2.5 g. of a new compound. This substance, from a consideration of its composition, rotation, and lack of reducing action toward Fehling's solution, must be the desired anhydride of altrose, and accordingly is named D-altrosan. It is readily soluble in water and in methyl alcohol, sparingly soluble in absolute ethyl alcohol. It was recrystallized as colorless, transparent prisms by allowing its methyl alcohol solution to evaporate in a desiccator over granular calcium chloride. The melting point of Daltrosan in a capillary tube appeared to be about 135°, after considerable preliminary sintering; however, a microscopic examination indicated that the probable melting point lies between 80 and 90°, the tiny melted particles being too viscous to coalesce until the higher temperature is reached. The rotation of D-altrosan, $[\alpha]^{20}D$ – 215° in water (c, 1), is close to the -220° estimated "from the rotation of D-altrose $(+32^{\circ})$ and the value -98° for the equilibrium mixture containing 43% D-altrose." Heated for two and one-half hours at 98–100°, a solution of D-altrosan in N hydrochloric acid (c, 1) became strongly reducing toward Fehling's solution, and changed in rotation to $[\alpha]^{20}$ D-109.1°; calculated as altrose, this value becomes -98.2° , in perfect agreement with the rotation -98.2° previously reported for D-altrose heated with acid under the same conditions. Anal.² Calcd. for C₆H₁₀O₅: C, 44.44; H, 6.22. Found: C, 44.46; H, 6.30.

The study of D-altrosan, and particularly the (2) Through the kindness of Dr. W. T. Haskins of this Laboratory.

allocation of the positions of its two rings, is being continued.

NATIONAL INSTITUTE OF HEALTH NELSON K. RICHTMYER WASHINGTON, D. C. C. S. HUDSON RECEIVED DECEMBER 12, 1938

THE REACTION OF ESTERS WITH SODIUM IN LIQUID AMMONIA

Sir:

The condensation of esters to acyloins by the action of sodium hitherto has been assumed to proceed in two stages: first, the reduction of the ester to the diketone and, second, the reduction of the diketone to the acyloin [Snell and McElvain, THIS JOURNAL, 53, 750 (1931)]. Our observations on the action of sodium on esters in liquid ammonia solution have yielded additional information concerning the intermediate products and enable us to offer some alternative mechanisms.

Blicke [ibid., 47, 229 (1925)] already has suggested that an ester reacts with one equivalent of sodium in an inert solvent to give a free radical and its dimer with which it is in equilibrium. The dimer can lose sodium alcoholate to give a diketone. This formulation is indicated in line 1 of the chart.

We have observed that when esters such as ethyl isobutyrate, ethyl benzoate, or ethyl trimethylacetate are introduced slowly into liquid ammonia containing two equivalents of dissolved sodium, an energetic reaction ensues without evolution of hydrogen. Upon removal of the liquid ammonia, in vacuo, solids are obtained which are spontaneously inflammable in air. These solids are thought to consist of compounds of the structure (I) in the chart, possibly contaminated with the sodium salts of the acyloins (II). These structures are indicated by the reactions of the solids with water to yield a mixture of the corresponding aldehyde and acyloin, and with alkyl halides, the corresponding ketones. Thus, specifically, ethyl benzoate reacts with two equivalents of sodium in liquid ammonia to give a deep red solution. Upon evaporation of the ammonia, a solid is obtained which is spontaneously inflammable in air and which reacts with water to give benzaldehyde and benzoin, with ethyl bromide to give propiophenone, with butyl bromide to give valerophenone, and with benzyl chloride to give desoxybenzoin. That the sodium salt of an acyloin can give a mixture having such properties,

i. e., that (II) can yield (I), was shown by treating the sodium salt of benzoin in liquid ammonia with two equivalents of sodium ethylate. A red solution was obtained which, on removal of the ammonia, yielded a solid which underwent the reactions noted above. We suggest, therefore, that the reduction of esters by sodium is more completely and accurately represented by the following scheme than by previous ones





It seems likely that the disodium compound (I) might react directly with a molecule of ester to give a diketone (III) or its sodium ethylate addition product (IV). This work is being continued and a full account will appear in the near future. GEORGE HERBERT JONES LABORATORY M. S. KHARASCH UNIVERSITY OF CHICAGO E. STERNFELD CHICAGO, ILLINOIS F. R. MAYO RECEIVED OCTOBER 29, 1938

THE BROMINATION OF TRIMETHYLETHYLENE Sir:

The dominance of the substitutive reactions of chlorine with isobutene over the addition process has long been known.1 In the course of studies² on the chlorination of olefins in a dynamic system, we observed that with flows of 50 cc./minute chlorine-100 cc./minute isobutene through a clean glass tube $(45 \times 1.3 \text{ cm.})$ thermostated at 70°, analysis of the effluent gases from the essentially liquid phase reaction showed 99% of the chlorine reacting, 93% by substitution. Distillation of the product roughly confirmed this; the results were (in weight per cent.): 75% 2-methyl-3-chloropropene-1 (methallyl chloride); 4% 2-methyl-1-chloropropene-1 (isocrotyl chloride); 5% dichlorides (1% unsaturated, 4% saturated); and 16% bottoms (4% unsaturated,

(1) Sheskukov, J. Russ. Phys.-Chem. Soc., 16, 478 (1884); Pogorshelski, *ibid.*, 36, 1129 (1904); Kondakov [*ibid.*, 17, 290 (1885)] observed a similar reactivity for trimethylethylene.

(2) Soon to be published,