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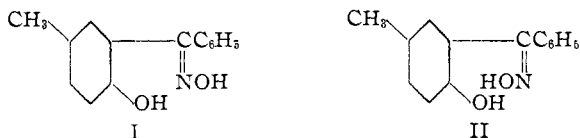
 COMMUNICATIONS TO THE EDITOR
 

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 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  
 WASHINGTON, D. C.

A. H. BLATT

RECEIVED DECEMBER 16, 1938

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 CRYSTALLINE D-ALTROSAN<sup>1</sup>

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  $-98^\circ$ ; 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-altroic 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 D-altrosan in a capillary tube appeared to be about  $135^\circ$ , after considerable preliminary sintering; however, a microscopic examination indicated that the probable melting point lies between  $80$  and  $90^\circ$ , the tiny melted particles being too viscous to coalesce until the higher temperature is reached. The rotation of D-altrosan,  $[\alpha]^{20}_D - 215^\circ$  in water (*c*, 1), is close to the  $-220^\circ$  estimated "from the rotation of D-altrose ( $+32^\circ$ ) and the value  $-98^\circ$  for the equilibrium mixture containing 43% D-altrose." Heated for two and one-half hours at  $98-100^\circ$ , a solution of D-altrosan in *N* hydrochloric acid (*c*, 1) became strongly reducing toward Fehling's solution, and changed in rotation to  $[\alpha]^{20}_D - 109.1^\circ$ ; calculated as altrose, this value becomes  $-98.2^\circ$ , in perfect agreement with the rotation  $-98.2^\circ$  previously reported for D-altrose heated with acid under the same conditions. *Anal.*<sup>2</sup> Calcd. for  $C_6H_{10}O_5$ : 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

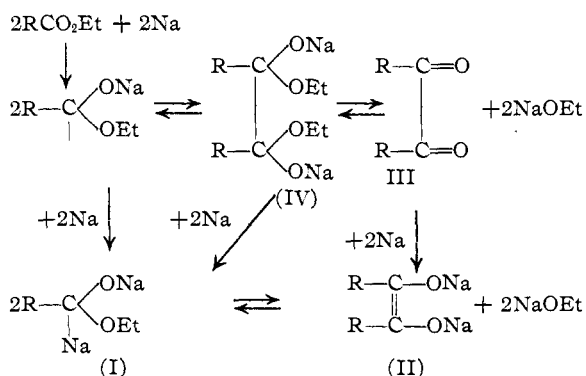
Sir:

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.<sup>1</sup> In the course of studies<sup>2</sup> 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 × 1.3 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.

12% saturated). However, packing the reactor with 44 g. of granular calcium chloride and operating at a higher temperature (109°) to avoid condensation, altered the results greatly; analysis of the effluent gas revealed complete disappearance of chlorine and that, seemingly, 19% of it reacted by substitution, producing hydrogen chloride. On this basis alone it would seem that 81% of the halogen was reacting by addition. The anomaly is explained readily by the distillation analysis, which showed that the product consisted of 38% (by weight) *t*-butyl chloride, 23% unsaturated monochlorides, 9% isobutene dichloride, 15% unsaturated dichlorides, and 15% trichlorides. It is seen that much hydrogen chloride produced by the substitutive reactions is added catalytically to isobutene (present in excess) to give *t*-butyl chloride, and thus is removed from the system. Interpretation of the distillation data gives 22% of the chlorine substituting and remaining as hydrogen chloride, which agrees fairly well with the 19% found by titration analysis.

In the light of the foregoing, the validity of the recent precise calorimetric measurement by Conn, Kistiakowsky and Smith<sup>3</sup> of the heat of the catalytic addition of bromine to trimethylethylene, a tertiary olefin, is subject to scrutiny. These workers in the course of their studies of such additions to olefins tested the effluent gas stream for unreacted halogen and for substitution by means of starch-iodide and congo red test papers and relied on refractive indices as criteria of purity of their products. Unfortunately, there is no literature value for trimethylethylene dibromide. By such tests they detected the occurrence of substitution during dynamic bromination of isobutene and cyclohexene and abandoned the experiments. However, trimethylethylene seemed to react cleanly, although some difficulty was experienced. We have attempted to confirm the work on the latter compound, inasmuch as it is so intimately related to our earlier studies.

Through a 45 × 1.3 cm. reactor thermostated at 82° and filled with 11 g. of 30% calcium bromide-70% asbestos were flowed the following vapors (in cc./minute): 24 Br<sub>2</sub>,<sup>4</sup> 300 trimethylethylene,<sup>5</sup> 240 N<sub>2</sub>, and 50 CO<sub>2</sub>. No

unreacted bromine or acid in the effluent gases was detectable with the test papers. After the experiment, inspection of the catalyst showed no contamination by liquid condensate. The product was carefully topped to remove all condensed unreacted olefin (*n*<sub>D</sub><sup>20</sup> 1.3870) and the residue (55 cc., 80 g., *n*<sub>D</sub><sup>20</sup> 1.4893) distilled in a small vacuum-jacketed column at 26.5 cm. pressure to reduce thermal decomposition. The following table summarizes the results and while no claim is made for cleanness of separation, it is shown definitely that the product of bromination is a mixture.

Cut no.	Range, °C.	Cc.	<i>d</i>	<i>n</i> <sub>D</sub> <sup>20</sup>	Bromine <sup>6</sup> no.
1	71.2-77.2	7.0	1.20	1.4448	18 (?)
2	77.2-92.2	9.5	1.22	1.4591	58
3	92.2-109.0	6.0	1.25	1.4838	89
4	Bottoms	31.0	1.7	1.5076	3.5

Cut No. 1 is probably principally *t*-amyl bromide<sup>7</sup> formed by addition of HBr to the olefin present in excess. The complete removal of the HBr is easily understood in view of the increase of reactivity of such olefins with increasing alkyl substitution on the ethylenic stem. Cuts 2 and 3 were extremely lachrymatory and are probably unsaturated bromides.<sup>8</sup> The bulk of Cut 4 (bottoms) is most likely saturated dibromide,<sup>9</sup> the addition compound and possibly one formed by substitution followed by addition of HBr.

Our results, while too crude to permit any reliable estimate of the true heat of additive bromination of trimethylethylene on the basis of the rules deduced, show the difficulty of avoiding substitutive reactions when halogenating tertiary olefins.

(6) Bromine numbers by Francis' method; g. Br<sub>2</sub>/100 g. sample.

(7) "I.C.T.," Vol. I, p. 277, *n*<sub>D</sub><sup>20</sup> 1.4421; Vol. I, 193, *d* 1.190.

(8) For comparison, 5-bromopentene-1 has *n*<sub>D</sub><sup>20</sup> 1.4640. Landolt-Börnstein, Vol. IIIB, p. 1685.

(9) For comparison, *n*<sub>D</sub><sup>20</sup> 1.5094 and *d* 1.7087 for 2,3-dibromopentane; "I.C.T.," Vol. I, p. 278, 192.

SHELL DEVELOPMENT COMPANY      WILLIAM E. VAUGHAN  
EMERYVILLE, CALIFORNIA          FREDERICK F. RUST

RECEIVED DECEMBER 19, 1938

## THE BROMINATION OF TRIMETHYLETHYLENE

Sir:

The authors of the preceding letter<sup>1</sup> were kind enough to acquaint us with its contents before publication. While we cannot in general dispute the correctness of their criticism, we believe that the errors thus introduced into our results<sup>2</sup> are

(1) Vaughan and Rust, THIS JOURNAL, 61, 215 (1939).

(2) Conn, Kistiakowsky and Smith, *ibid.*, 60, 2764 (1938).

(3) Conn, Kistiakowsky and Smith, THIS JOURNAL, 60, 2764 (1938).

(4) Baker Analyzed c. p. grade.

(5) 100% olefin; *n*<sub>D</sub><sup>20</sup> 1.3867; compare with 1.3869 by Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, 68, 141 (1936).

rather small because of the following circumstances.

The catalyst we used in the bromination of trimethylethylene was rather inactive because of extended previous use so that, for instance, it failed to brominate ethylene completely after the experiments on trimethylethylene. Thus the secondary reactions described in the preceding article may easily have been less pronounced in our experiments. This is, indeed, borne out by the agreement of the refractive index of our product with that calculated from atomic refractivities for trimethylethylene<sup>3</sup> and roughly with that found by Vaughan and Rust for their high boiling fraction. It is safe therefore to conclude that the yield of monobromides in our experiments was quite small.

(3) Calcd. 1.5050 from Hückel, "Theoretische Grundlagen der organischen Chemie," 2. Auflage, 2 Band, p. 86; obsd. 1.5054 = 0.0003; high boiling fraction of Vaughan and Rust, 1.5076.

Since there was no halogen acid in the exit gases the reaction  $C_5H_{10}Br_2 \rightarrow C_5H_9Br + HBr$  must have been followed quantitatively by the reaction  $C_5H_{10} + HBr \rightarrow C_5H_{11}Br$ . Thus these secondary reactions can be combined into one reaction  $C_5H_{10}Br_2 + C_5H_{10} \rightarrow C_5H_{11}Br + C_5H_9Br$ , the heat of which, according to our present information, is quite small. Hence even a considerable yield of monobromides could not have seriously affected our thermal data.

In view of all this we still believe that our estimate (200 cal./mole) of the over-all error is adequate although the observed variations of the refractive index of the product suggest that small variable quantities of the monobromides might have been present.

CHEMICAL LABORATORIES  
HARVARD UNIVERSITY  
CAMBRIDGE, MASS.

JOHN B. CONN  
G. B. KISTIAKOWSKY  
ELGENE A. SMITH

RECEIVED DECEMBER 19, 1938

## NEW BOOKS

**Unit Processes in Organic Synthesis.** By P. H. GROGINS, Editor-in-Chief, Senior Chemist, Bureau of Chemistry and Soils, United States Department of Agriculture. Second edition. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York, N. Y., 1938. xiii + 769 pp. Illustrated. 16 × 23.5 cm. Price, \$6.00.

The general plan of this second edition is essentially unchanged from that which was followed in the first edition. Every chapter has been revised and an attempt has been made to bring each into line with current developments as revealed by the technical and patent literature. Worthy of mention in this respect is the augmenting of the chapter on Diazotization to include Coupling; the chapters on Alkylation and Polymerization have been enlarged; increased emphasis has been laid on the synthesis of aliphatic compounds; a substantial number of new flow sheets has been incorporated; sections explaining the theoretical basis of halogenation and hydrogenation reactions by means of thermodynamics have been introduced.

In this book some of the more important general reactions (nitration, amination by reduction and ammonolysis, diazotization and coupling, halogenation, sulfonation, oxidation, hydrogenation, alkylation, esterification, hydrolysis, Friedel and Crafts reaction, polymerization) of commercial interest to the organic chemist are first discussed. Following this is a detailed description of the reagents, the various physical conditions as they affect the course of the reactions involved and the types of com-

pounds which may be satisfactorily prepared with these reagents. Finally, the design and construction of equipment that has been successful for the various reactions are described followed by procedures that may be used for synthesizing on a large scale one or more typical compounds of each class.

Of necessity, the general discussion of the reactions has been condensed and limited to the more important facts such as are presented in a first year course in organic chemistry. The inclusion of organic chemical theory naturally has been even more limited. In enumerating the reagents the more important of both scientific and practical significance have been included. This sort of information collected as it is in a relatively few pages and supplemented by original references is valuable to chemists and chemical engineers and may be referred to frequently by research chemists, who are using these reactions. The larger scale equipment, frequently with flow sheets, is of primary interest to the chemical engineer though a well-rounded chemist should also have some knowledge of equipment if he is studying reactions for industrial development. The examples of syntheses have been well selected and a large proportion of them are for products which have been marketed only during the past few years. The mere fact that the description of such processes in many cases is taken from patents, and hence probably does not coincide in all details with the actual operations carried out by the producer, does not detract from its value to the industrial chemist. The economic factors discussed